THE PHYSICAL SOCIETY

1926-27.

I.—THE ABSORPTION OF RADIATION IN THE UPPER ATMOSPHERE.

The Eleventh Guthrie Lecture. Delivered April 23, 1926.

By Prof. Charles Fabry.

(Translated from the Lecturer's manuscript by the Assistant Secretary.)

THE subject upon which I propose to address you is far from being a new one. It is, however, topical, for several new and interesting facts have been added to our knowledge of it in recent times, and since these discoveries have been followed with as much interest in England as in France, while I have myself contributed directly or indirectly to their study, it seemed to me that the question would be a suitable one for a lecture given by a French physicist before a British society.

Limitation of the Solar Spectrum.

The subject dates from the discovery of the limitation of the solar spectrum. Whatever the apparatus employed and whatever the height at which the observations are taken, it is impossible to detect in that spectrum any radiation of a wavelength less than about 2900 Å.U., and further investigations have shown that a similar limitation characterizes the spectra of all the stars. Moreover, since the limit shifts in the direction of increasing wavelength as the sun recedes from the zenith, the assumption naturally follows that the limitation is produced by absorption in the earth's atmosphere. A careful study of the question, made by Cornu[*] in 1881, led to the conclusion that the absorption is due to a permanent component of the atmosphere, and not to a very variable component such as water vapour or carbon dioxide ; however, the absorption underwent slight variations from day to day. The nature of the absorbing component could not then be determined: As to its distribution in the atmosphere, Cornu did not rule out the lower strata : he even seems to have believed that the gas in question was uniformly distributed in altitude.

Almost at the same time, Hartley discovered that ozone has a strong absorption band in the ultra-violet, and attributed the limitation of the solar spectrum to this gas. In the absence of any numerical data his explanation remained hypothetical : chemical analysis of the lower atmosphere revealed the presence of ozone in such small quantities that its influence on the absorption remained doubtful.

In consequence of the researches of Miethe and Lehman[†] in 1909, doubt was thrown on the very existence of radiation of short wavelength in the energy emitted by the sun. These workers studied the solar spectrum at a series of successively higher altitudes, and established the fact that the limit at the ultra-violet end remained practically the same in all cases. Without denying the existence

---

[*] Cornu, Sur l'absorption atmosphérique des radiations ultra-violettes ; Journal de Physique, Série 1, Vol. 10, p. 5 (1881). Sur la limite ultra-violette du spectre solaire, etc., Comptes Rendus de l'Académie des Sciences, Vol. 111, p. 941 (1890).

[†] Sitzungsberichte de Kön. Preus. Akad. der Wiss, Vol. 1, p. 268 (1909).

of atmospheric absorption (which is demonstrated by the fact that the limit of the spectrum shifts as the sun recedes from the zenith), they thought that there must also be strong absorption in the atmosphere of the sun, all radiation of wavelength less than 2900 being thereby completely cut off.

It was necessary, therefore, in order to carry further the study of this question, to introduce numerical data, instead of relying on merely qualitative methods. This work was begun in 1912 by M. Buisson and myself, and has since been continued by several other physicists.

ABSORPTIVE PROPERTIES OF OZONE.

Since ozone is supposed to be responsible for atmospheric absorption in the ultra-violet, it is necessary in the first place to know the absorptive properties of this gas. Its absorption of other parts of the spectrum also is interesting, for if the presence of ozone be demonstrated, all its absorption bands ought to be found in the solar spectrum.

The absorptive properties of ozone may be summarized as follows, the bands being arranged in order of increasing wavelength :—

(1). A very strong absorption band in the ultra-violet, the most intense part of which extends from 2300 to 3100, with a maximum at 2550. This band is continuous, without any structure. It may be referred to as the Hartley band.

(2). A complicated group of bands at the end of the preceding band, roughly between 3100 and 3500. These may be called the Huggins bands, since Huggins observed them for the first time in stellar spectra, although he was not aware of their origin.

(3). A group of bands discovered by Chappuis in 1882 and situated in the visible region, chiefly in the yellow and the red. The absorption in this case is much less marked than in the case of Group (2), being clearly observable only where a considerable depth of ozone is passed through.

(4). Bands in the infra-red, between 4μ and 7μ, about which scarcely anything is known.

Up to the present time, bands (1), (2) and (3) have been observed in the solar spectrum, and all of them have led to interesting results. The infra-red bands have not been observed.

THE HARTLEY BAND.

When I began, with M. Buisson, to concern myself with this question, adequate numerical data as to the absorption coefficients of ozone did not exist. We had first of all to measure these coefficients for the Hartley band.*

This determination was made by the method of photographic photometry. The source of light was a quartz mercury lamp, and the absorption was determined for all the mercury lines between 3300 and 2300. The coefficient of absorption α is defined by the equation

$$I = I_0 \cdot 10^{-\alpha x}$$

where x is the depth in centimetres of pure gaseous ozone traversed by the radiation, while I_0, I, are the intensities of the incident and transmitted radiation respectively.

---

* Fabry et Buisson, L'absorption de l'ultra-violet par l'ozone et la limite du spectre solaire, Journal de Physique, série 5, Vol. 3, p. 196 (1913).

We may also write

$$a = 1/x \, \log_{10}(I_0/I)$$

The quantity $\log_{10}(I_0/I)$ may, as is usual in photographic technique, be called the *optical density* of the absorbent layer : the coefficient a may then be defined as the optical density of 1 cm. of pure gaseous ozone.

We have determined the values of a by a photographic method. For the purpose of reducing intensities as required diaphragms were placed over the objective of the spectrograph, while the degree of blackening of the plate was measured by means of our micro-photometer.* The result of these measurements is represented by the curve shown in Fig. 1, which gives the values of a as a function of the wavelength. It is easy to recognise the form of the absorption curve, which regularly occurs in broad bands, and there is a very pronounced maximum at $\lambda = 2550$. The maximum value of a reaches 123, an exceptionally high figure. A layer of pure
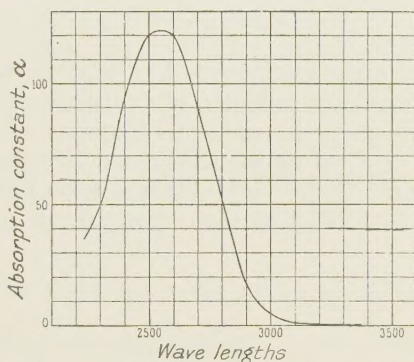
FIG. 1.

gaseous ozone 25μ in thickness would reduce by one-half the intensity of radiation of wavelength 2550, and if the ozone could be reduced in volume so as to have the density of silver, the same result would be obtained with a layer $5m\mu$ in thickness. It may be said that, in this region, the absorption by ozone is metallic in character.

For the study of atmospheric absorption, the interesting part of the curve is that which extends to the right of the maximum, roughly between 2800 and 3200. Within this region, the values can be expressed by the following empirical formula :†

$$\log a = 17 \cdot 58 - 0 \cdot 00564\lambda \qquad \ldots \ldots \ldots \ldots (1)$$

the wavelength λ being expressed in Ångströms.

I think it would be useful to make these measurements more complete in certain respects. At its long wavelength end the Hartley band joins the Huggins bands, of which we were not aware when our measurements were made : the curve descends in a less regular manner than is indicated by the preceding formula. Further, it

---

* Revue d'Optique, Vol. 3, p. 1 (1924).

† I have had occasion to establish the fact that an analogous formula represents the descending part of the absorption curve with sufficient accuracy in the case of a great many broad bands.

would be interesting to find out for certain that the coefficients of absorption do not change with temperature and are not modified by the admixture of various gases with the ozone.

THE MEASUREMENT OF THE ATMOSPHERIC COEFFICIENTS OF ABSORPTION.

In order to compare the atmospheric absorption with that of ozone and to verify the hypothesis put forward by Hartley, it is necessary to measure numerically the values of the atmospheric coefficient for radiations of various wavelengths, that is, to apply to the atmosphere the method which has just been explained as applied to ozone. If the two absorption curves coincide, we may feel certain that the absorption is due to ozone, and at the same time we shall have a measure of the quantity of this gas contained in the atmosphere.

The coefficient m of atmospheric absorption is defined by the equation

$$m = \log (I_0/I)$$

where I_0 is the intensity of the radiation before it passes through the atmosphere, and I is the intensity of the same radiation when it reaches the earth, the sun being at the zenith. As the quantity I_0 cannot be measured directly, the only way to measure m is to vary the depth of air passed through, by observing the sun at various heights above the horizon. If the sun's distance from the zenith be z, the depth of air passed through is multiplied by sec z, and the intensity I which reaches the earth is given by

$$\log I = \log I_0 - m \sec z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The measurement of I for a series of values of z enables us to draw a graph in which the values of sec z are taken as abscissæ and those of log I as ordinates. The points obtained must lie on a straight line, the slope of which gives the coefficient m.

This is the well-known Bouguer-Langley method. It presents, however, certain special difficulties in the case we are considering, thus :—

(1). It is impossible to use the bolometric method, because the intensity of the radiation to be measured is too small after the solar spectrum has been weakened by atmospheric absorption.

(2). It is necessary to use for detecting the radiation an instrument giving very high definition, since the absorption varies very rapidly from point to point of the spectrum. A mean value taken over a short spectral range would have no meaning.

(3). The utmost care must be taken to eliminate from the radiation to be studied all that which comes from other parts of the spectrum. The latter is always in evidence on account of diffusion from the surfaces of the lenses and prisms.

The first two of the above considerations led us to employ the method of photo-metric photometry.

The third difficulty can be overcome in two different ways. Efforts may be made to eliminate the greater part of the undesired radiation by means of a suitably chosen absorbent : but the discovery of a suitable absorbent is a very difficult undertaking, and only a lucky chance can bring success in it. Cornu employed bromine vapour : Mr. Dobson has perfected this method, and has arrived at a

really satisfactory result by the use of a filter formed of two parts, one containing bromine vapour and the other chlorine vapour.*

We have adopted another solution of the problem, consisting in the use of a double spectograph† in which only quartz is employed. The first spectroscope is formed of two 60-degree prisms, P, P' (Fig. 2), and two lenses, L, L', having a focal length of about 1 metre. The spectrum is projected upon a horizontal slit S. This spectrum is contaminated by diffused light, the intensity of which is not negligible, on account of the enormous intensity in the solar radiation of the visible light and of the adjacent end of the ultra-violet spectrum. The second spectroscope gives a dispersion at right angles to the first, and purifies the spectrum ; it is formed of the two prisms p, p' and the lenses l, l'. Finally the spectrum, completely purified, is projected on to a photographic plate at T. In this way it is practicable to make exposures up to one hour for the solar spectrum without the use of any screen.

The intensity falls off extremely rapidly towards the shorter wavelengths at the extremity of the solar spectrum. The normal exposure with slow plates is
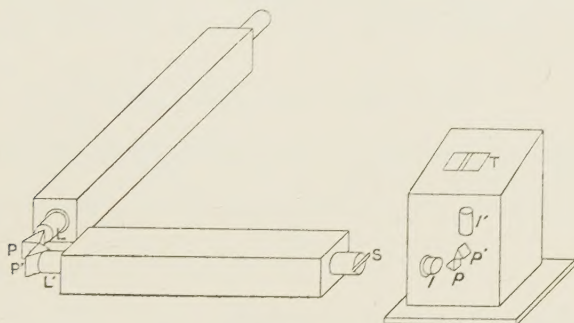

FIG. 2.

one minute for wavelengths in the neighbourhood of 2936 ; but with this exposure the plate is very much over-exposed for $\lambda=2975$, and for $\lambda=3100$ the normal exposure is 1/100 of a second. It would be impossible, therefore, to obtain the whole of the range with which we are concerned in a single exposure. This difficulty is overcome by covering the slit S with filters, which weaken a part of the spectrum. The region $\lambda<2990$ is left untouched ; the region lying between 2990 and 3060 is reduced to 1/100, and the region lying between 3060 and 3200 is reduced to 1/2000.

A series of exposures is made on the same plate at different hours of the day. At noon additional exposures are made with intensities reduced in known ratios

* The work of Messrs. Dobson and his collaborators has been described in several publications, of which the following is the latest and most complete : G. M. B. Dobson and D. N. Harrison, "Measurements of the Amount of Ozone in the Earth's Atmosphere," Proc. Roy. Soc., A, Vol. 110, p. 660 (1926).

† Ch. Fabry et H. Buisson, Etude de l'extrémité ultra-violette du spectre solaire," Journal de Physique, série 6, Vol. 2, p. 197 (1921).

by means of diaphragms, to enable the curve showing the rate of darkening of the plate to be traced, so that it may be possible to infer the intensities of the incident radiation from the corresponding densities on the plate. Measurements with the microphotometer (which take a long time and are very tedious) then make it possible to determine, for each wavelength, the intensity-ratios which obtain at different hours of the day.

Atmospheric absorption must be attributable to three causes :

(1). The principal absorption, which increases rapidly with diminishing wavelength, is due to the gas which we are seeking to identify with ozone.

(2). Molecular scattering in the air (Rayleigh's phenomenon) produces an absorption which can be exactly calculated for any given wavelength and solar elevation.

(3). Absorption is produced by the fog and dust contained in the air. This is practically independent of the wavelength over the small range which we are studying, but may vary in an unknown manner from hour to hour.

For a wavelength λ, let m be the coefficient of absorption, due to the unknown gas, and β that due to molecular scattering when the sun is at the zenith. If I_0 be the intensity of the radiation of wavelength λ before entering the atmosphere, the intensity I at the surface of the earth when the sun makes an angle z with the zenith will be given by

$$\log I = \log I_0 - (m+\beta) \sec z + \delta,$$

where δ is a number independent of λ, but varying irregularly during the day ; it represents absorption by fog and dust.

For a different wavelength λ' we shall have, at the same moment

$$\log I' = \log I_0' - (m'+\beta') \sec z + \delta.$$

Eliminating δ between these equations we have

$$\log I - \log I' = K - (m - m' + \beta - \beta') \sec z,$$

where K is a quantity independent of the time of day.

We take as λ' the longest wavelength in the region to be studied, so that λ' =3143, in which case the principal absorption coefficient m' is small. For each of the other wavelengths we draw a graph, taking as abscissæ the values of $\sec z$, and as ordinates those of $\log I - \log I'$. The curve obtained in this way must be a straight line, the slope of which gives the value of $(m - m' + \beta - \beta')$.

Fig. 3 shows a curve of this kind based on observations made on June 7, 1920. It will be seen that for each wavelength the points lie on a straight line, and that the slope of this line increases rapidly as the wavelength diminishes. This slope having been measured for each wavelength, the values of the quantity $(m - m' + \beta - \beta')$ are known ; further, the values of β and β' are known, so that the values of $m - m'$ can be calculated.

These results can then be compared with the absorption coefficients of ozone. Let us suppose that this gas is responsible for the atmospheric absorption, and let α and α' be the values of its absorption coefficient for wavelengths λ and λ' ; these values are given by equation (1). If x denote the total depth, expressed in centi-

metres, of pure gaseous ozone equivalent to the ozone distributed through the atmosphere, we have

$$m - m' = (a - a')x, \text{ or } x = \frac{m - m'}{a - a'}$$

If by means of this equation we calculate the value of x from data for a series of different wavelengths, we ought to obtain the same result in each case. The following table gives the figures for the data obtained on June 7, 1920. The column
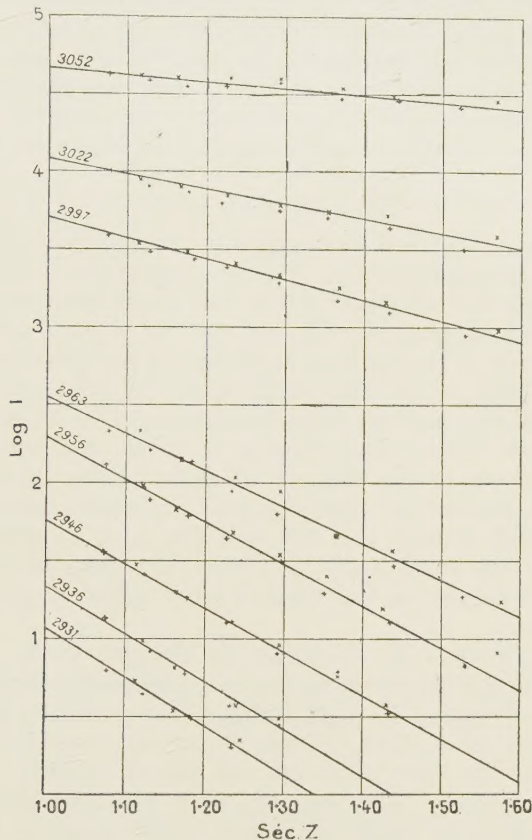

Fig. 3.

marked P gives the slope measured directly on Fig. 3, and the remaining columns contain quantities which have already been explained.

λ	β	$\beta-\beta'$	α	$\alpha-\alpha'$	P	$m-m'$	x
2931	0·47	0·11	11·2	10·5	3·15	3·04	0·290
2936	0·46	0·10	10·5	9·8	3·16	3·06	0·312
2946	0·46	0·10	9·3	8·6	2·78	2·68	0·312
2956	0·45	0·09	8·1	7·4	2·66	2·57	0·347
2963	0·45	0·09	7·4	6·7	2·37	2·28	0·340
2997	0·43	0·07	4·7	4·0	1·32	1·25	0·309
3022	0·42	0·06	3·4	2·7	0·96	0·90	0·333
3052	0·40	0·04	2·3	1·6	0·44	0·40	0·250
3143	0·36	0·00	0·7	0	0	0	...

It will be seen that the value found for x is practically constant,* and that the total thickness of the layer of ozone is a little more than 3 mm.

The hypothesis with regard to ozone has thus been completely confirmed. In other ways, also, it explains the facts well, and in particular it explains why it is quite impossible to observe radiation of short wavelength through the atmosphere. The shortest wavelength that it has been possible to record is 2885 ; the coefficient of absorption for 2898 (taking account of both ozone absorption and molecular scattering) would be 6·36—that is to say, the atmosphere allows one two-millionth part of the incident energy to pass through it when the sun is at the zenith. The importance of avoiding all extraneous illumination when recording such feeble intensities will be readily appreciated. It is probably out of the question to carry the investigation beyond this wavelength ; for $\lambda=2800$, the absorption by atmospheric ozone reduces the intensity to 10^{-15} of its original value.

THE HUGGINS BANDS.

These bands were observed by Huggins in the spectrum of Sirius, but he did not discover their terrestrial origin. The true explanation of their occurrence is due to Fowler and Strutt,† who showed that they are also observable in the spectrum of the sun when the latter is near the horizon. It is more difficult, however, to detect them in the case of the sun than in the case of the whiter stars, because in the neighbourhood of 3300, where these bands occur, the solar spectrum is filled with Fraunhofer lines, which render the ozone bands less clearly apparent.

These bands are entirely characteristic of ozone, and would be sufficient of themselves to demonstrate the presence of ozone in the atmosphere. They are not observed when the sun (or a star) is near the zenith, because the absorption is not then sufficiently intense, and this fact is in good accordance with measurements made in the laboratory of the absorption coefficients for the Huggins bands. A depth of atmosphere three or four times as great as that at the zenith renders the bands clearly visible.

An interesting method for observing the Huggins bands in the light which reaches us from the sun has recently been announced by Cabannes and Dufay.‡ It consists in photographing the light which comes zenithally from the sky when the sun is very near the horizon, or even during early twilight : in this way it is possible to examine the light which has not passed obliquely through the lower strata of the atmosphere. Now although, as is indicated below, there is strong absorption by ozone in the upper atmosphere, nevertheless, in this case, radiation of the ultra-violet range considered occurs in far greater proportion than in the case of radiation transmitted mainly through the lower atmospheric strata. The reason why the proportion is greater than for direct solar illumination is that the radiation coming from the sky has been scattered in accordance with the λ^{-4} law.

---

* Little importance should be attached to the value of x deduced from measurements of radiation of wavelength 3052, which is absorbed to such a slight extent that the resulting value of x is the quotient of two quantities too small to give a very precise result. The observations on 2931, also, are not very trustworthy ; in this case the atmospheric absorption is too strong and the radiation too weak for accurate measurements to be made.

† Proc. Roy. Soc., A, Vol. 93, p. 577 (1917).

‡ Mesure de l'altitude de la couche d'ozone dans l'atmosphère, Comptes-Rendus de l'Académie des Sciences, Vol. 181, p. 302 ; 24 août (1925). Also Journal de Physique (1927).

This method of observation has led to the discovery of several new bands, the wavelengths in which lie between 3445 and 3608. It is possible that these also belong to ozone, but this is not yet certain.

Chappuis Bands.

These bands, which occur in the visible spectrum, chiefly in the red and yellow regions, can only be observed with a great depth of ozone. Chappuis* used a tube 4·50 metres long, with an ozone concentration which was not measured, but was as strong as possible. Under these conditions the gas is blue in colour.

The coefficients of absorption have been determined in my laboratory by M. Colange : Fig. 4 gives the absorption curve. The maximum value of the coefficient is that for 6000—namely, 0·05 ; with this should be compared the value 123 for $\lambda=2550$. A layer of ozone 3·5 mm. deep would, when the sun is at the zenith, absorb only 4 per cent. of radiation of wavelength 6000.

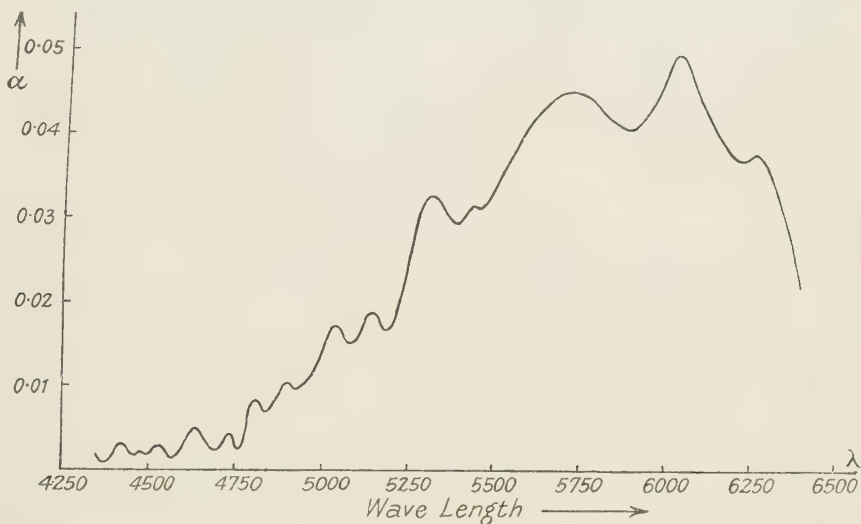The Chappuis bands have never been observed directly in the solar spectrum.

Fig. 4.

I have often looked for them in the spectrum of the setting sun, but have never found them. This is explained by the slightness of the difference between the maxima and minima of absorption (*see* the curve in Fig. 4), and also by the fact that in the neighbourhood of these bands the spectrum is filled with lines due to water vapour, which assume great importance when the sun is low.

However, the atmospheric absorption due to the Chappuis bands has recently been brought out by Cabannes and Dufay,† by inference from data which have long been known. The atmospheric coefficients of absorption were determined very exactly by Fowle from his observations at Mount Wilson.‡ These data cover the

* Chappuis, Annales de l'École Normale Supérieure, Vol. 11, p. 137 (1882), and Journal de Physique, série 2, Vol. 1, p. 494 (1882).
† Société Française de Physique, 2 juillet (1926). Journal de Physique, Sept. (1926).
‡ Astrophysical Journal, Vol. 38, p. 392 (1913), and Vol. 40, p. 435 (1914).

infra-red, the visible spectrum, and the beginning of the ultra-violet ; they have been corrected by allowing for the effect of water vapour. Fowle remarked that molecular scattering explains the greater part of the atmospheric absorption which has been corrected in this way, but that there is a residual selective absorption chiefly in the red and the yellow. Cabannes and Dufay have shown that this residual absorption is that of ozone in the Chappuis bands. They employed a diagram due to Fowle ; since the absorption coefficient for molecular scattering varies as λ^{-4}, a graph is drawn with values of λ^{-4} as abscissæ and values of the absorption coefficient as ordinates,* and in this way the curve shown in Fig. 5 is obtained.
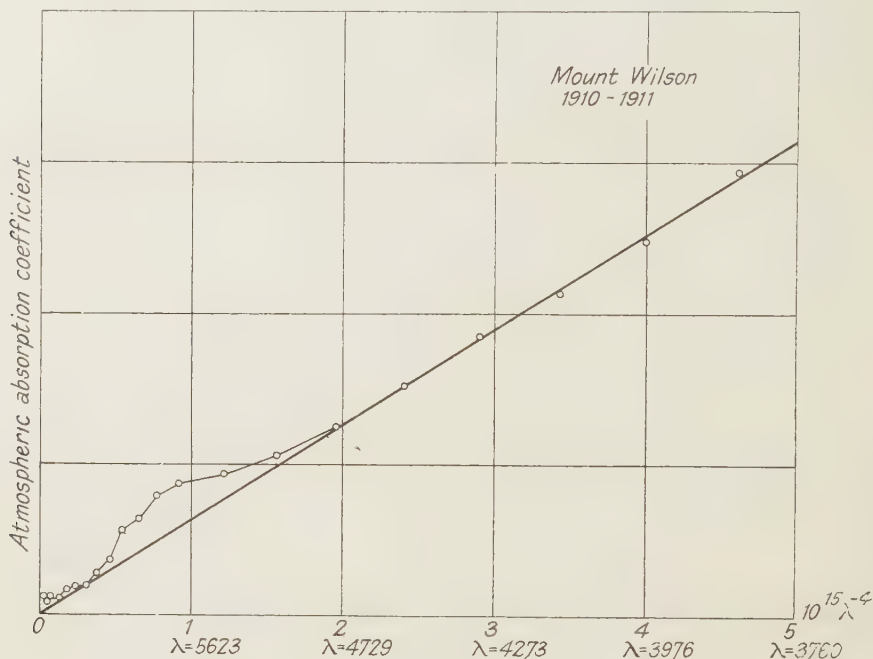

FIG. 5.

Throughout the greater part of the spectrum the points lie on a straight line, but at one place the curve breaks clearly away from the line, and it is exactly in this region that the Chappuis bands occur. The differences between the ordinates of the curve and those of the straight line must represent the coefficient of absorption of atmospheric ozone. In order to see whether this is really the case, the ordinate differences obtained in this way are used to calculate the values of the absorption coefficients of ozone (for the standard depth of 1 cm.) on the assumption that the depth of the atmospheric layer of ozone is 0·32 cm. The values so found are shown as a function of the wavelength in Fig. 6, where each individual point is deduced from one of Fowle's results, while the continuous curve is that of Colange (Fig. 4). The points lie on the curve with a precision which is truly remarkable, when it is

---

* In defining the absorption coefficient, Fowle employs Napierian instead of ordinary logarithms.

considered that the starting point was the very difficult measurements of atmospheric absorption made by Fowle, and that the absorption by ozone constitutes only a small part of the absorption so measured.

By treating in the same way the absorption measurements made at Mount Wilson in various years, Cabannes and Dufay believe that they can show variation in the quantity of ozone present in the atmosphere.

INFRA-RED BANDS.

These bands have never been observed in the solar spectrum; they probably lie in a region where the latter cannot be observed. It has, however, been supposed that they play a certain part in meteorological phenomena by absorbing a part
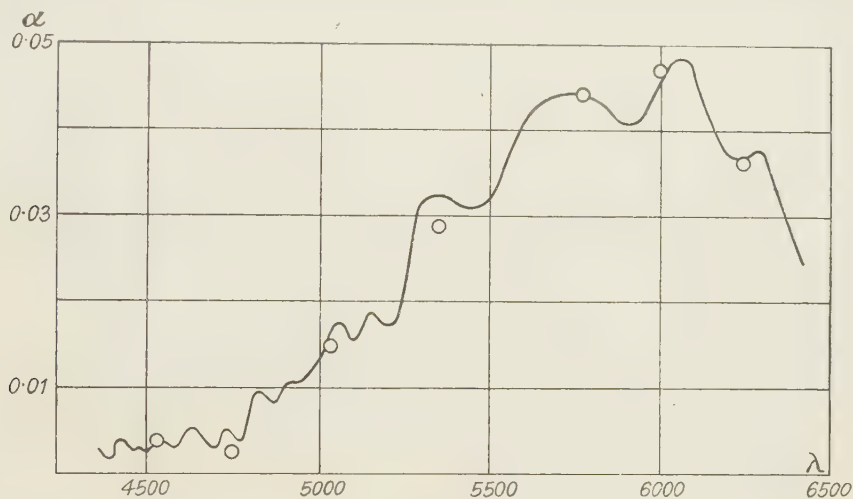

FIG. 6.

of the radiation given out by the earth into space. No numerical value of the absorption coefficients is known, and it is impossible to say whether the supposed effect is real or negligible.

LOCATION AND ORIGIN OF ATMOSPHERIC OZONE.

The preceding observations give no information as to the distribution of ozone in the atmosphere. If the layer of 3 mm. were uniformly distributed, the proportion of ozone would be 4×10^{-7} by volume, or 60 mg. per 100 kg. of air by weight.

The chemical estimation of very small quantities of ozone appears to be a very uncertain operation. The most reliable measurements give proportions of this gas very much lower than the figures I have just mentioned. Lespieau* finds, at the surface of the earth, 3 mg. of ozone per 100 kg. of air; he finds the same proportion at the top of Mount Blanc, at a height of 4,800 metres.

An optical method of estimating the ozone in accessible layers of air was suggested in 1912 by M. Buisson and myself. It was to consist in studying the absorption in these layers with a source of light rich in ultra-violet rays, such as a

* Lespieau, Bulletin de la Société chimique de Paris, série 3, Vol. 35, p. 616 (1906).

mercury lamp. The experiment was carried out in 1918 by R. J. Strutt,* who found that the mercury line 2536 could be transmitted through 6·5 km. of air. If the ozone were uniformly distributed through the atmosphere, a layer of this depth would only transmit 10^{-33} of the radiation in question. It would be interesting to repeat this experiment in various places and to calculate from the absorption the proportion of ozone present in each case.

It is certain, then, that the quantity of ozone disclosed by the study of the solar spectrum is not furnished by the lower atmosphere, or even by the part of the atmosphere which is accessible on a mountain. The same conclusion follows from the fact that the limits of the solar spectrum do not alter appreciably when observations are taken at the greatest accessible altitudes. The inference is, therefore, forced upon us that the ozone occurs principally at extremely high altitudes. A theory as to the manner in which it is formed may be propounded as follows :—

Radiation of very short wavelength ($\lambda < 1850$) acts upon oxygen, transforming it into ozone ; at the same time this radiation is strongly absorbed by the air. It is probable that such radiation exists in the solar emission ; it must produce ozone in the earth's atmosphere, but only in the highest part, because it cannot reach the lower strata. Radiation of $\lambda = 1850$ is completely absorbed by 10 metres of air at atmospheric pressure, and could scarcely penetrate lower than the stratum 40 km. above the earth. On the other hand, radiation lying between $\lambda = 2000$ and $\lambda = 3000$ decomposes ozone, and between these two inverse actions a state of equilibrium must be established, the quantity of ozone depending on the relative intensities of the two ranges of radiation. We shall come back a little later on to the question of variations in the quantity of ozone. It would be extremely interesting to be able to determine the height at which the greater part of the gas is to be found. Experiments at the top of a mountain and even experiments with balloons have hitherto given no result. Together with M. Buisson, however, I have suggested the following method for attacking this problem :—

The law (equation (2)), according to which sec z represents the falling off of intensity as the zenithal distance increases, neglects the curvature of the earth. It remains accurate so long as the zenithal distance is not great, but it is no longer exact when the sun approaches the horizon. The upper strata are then traversed less obliquely than the lower strata, and the falling off is slower than is indicated by the equation. The divergence from equation (2) increases with the height at which the absorbing layer is located. In other words, if we draw the graph giving log 1 in terms of sec z we shall obtain a straight line if the absorbing gas be at a low altitude, the graph departing from linearity in an increasing degree as the altitude of the gas increases.

This method has recently been carried into effect by MM. Cabannes and Dufay,† by measuring the Huggins bands in the light scattered from the sky in a zenithal direction, with the result that the ozone is found to occur at a height of some 50 kilometres. This result can only be approximate, for the ozone is certainly not restricted to a shallow layer, but distributed over a considerable depth above a certain altitude. The conclusion is reached, however, that the absorbing layer lies very much higher than the altitudes which can be reached by means at our disposal.

---

* Proc. Roy. Soc., A, Vol. 94, p. 260 (1918).
† Comptes-Rendus, loc.cit.

The Radiation Emitted by the Sun.

It is only by extrapolation that we can obtain any information as to the radiation emitted by the sun for the range of wavelengths below 2885, of which no trace reaches us. The hypothesis has been put forward by Miethe and Lehmann that this radiation does not exist, in consequence of absorption in the solar atmosphere. According to these authors the range in the neighbourhood of 2900 is also greatly weakened by such absorption.

This question was studied by M. Buisson and myself after investigating the laws of absorption by the earth's atmosphere. By comparison with the radiation from the crater of the electric arc, assumed to be identical with the radiation of a black body at 3750 K, we obtained the spectral intensity curve for the solar spectrum for the range 3150-2898, applying to the observed values a correction for atmospheric absorption. In consequence of the Fraunhofer lines there are fluctuations from point to point in the actual solar spectrum, but there is no such marked discrepancy as would be expected if the solar atmosphere suppressed the short-wave length range.

The same conclusion is reached on comparing the spectrum of radiation coming from the centre with that coming from the circumference of the sun. If the solar atmosphere contained a layer sufficiently absorbent to eliminate the range $\lambda < 2880$, such absorption would be much more marked at the edge of the sun's disc than at the centre, and the ultra-violet limit would be seen to advance on passing from the centre to the circumference. We have made the comparison by means of our double spectrograph, and we have found no appreciable difference of this kind. The spectrum for the circumference is weaker than that for the centre, but the limit is the same.

There is reason, therefore, if we extrapolate from these results, to believe that the energy curve for the radiation emitted by the sun resembles, in the ultra-violet region no less than in other parts of the spectrum, that of a black body in the neighbourhood of 6000 K. If so the intensity must retain a very considerable value right up to the Schumann region, and this is in fact what is assumed in the theory of the formation of ozone which has been explained above.

Duclaux and Jeantet have pointed out[*] that the ozone layer absorbs strongly the radiation comprised between 2900 and 2200, but that for wavelengths less than this limit it becomes transparent once more, so that we ought to receive the radiations comprised between 2200 and 2000 if ozone were the only absorbent gas. They have tried to find out whether any other gas could absorb this range of radiation, and have ascertained that ammonia possesses a very intense absorption band in the region in question. The quantity of ammonia existing in the lower atmosphere in consequence of the decomposition of organic matter is supposed to be sufficient to cut off this radiation completely. If this theory were correct, we should be screened from radiation in the range 2900-2200 by the ozone of the upper atmosphere, and from the range 2200-2000 by the ammonia of the lower atmosphere. At the top of a high mountain it would be possible to detect the latter range.

This question has been investigated by MM. Chalonge, Déjardin and Lambert during an ascent of Mont Blanc, by means of a double spectrograph specially designed to ensure the complete elimination of diffused light.[†] They employed oiled plates,

---

[*] Duclaux et Jeantet, Journal de Physique, série 6, Vol. 4, p. 115 (1923).
[†] Revue d'Optique, Vol. 3, p. 277 (1924).

in accordance with the technique described by Duclaux and Jeantet,* and also Schumann plates. No trace of radiation in the region 2200-2000 could be found. The question, therefore, remains unsettled. Possibly oxygen in great depth is sufficiently absorbent to explain the absence of such radiation.

Variations in the Quantity of Atmospheric Ozone.

Cornu noticed that the limit of the solar spectrum, for a given zenithal distance of the sun, varies from day to day in an irregular manner. M. Buisson and I have observed the same fact, and have come to the conclusion that there is a variation in the quantity of atmospheric ozone. Our method gives for each day the thickness of the ozone layer reduced to atmospheric pressure. On a series of 14 days during 1920 we found values ranging from 2·85 to 3·35 mm. These values are much in excess of the probable error of the observations, and we confirmed them by means of a series of spectra taken on the same plate at noon on several consecutive days.

This question has recently aroused keen interest. An extensive research has been undertaken by Messrs. Dobson and Harrison,† who believe that they have found a connection between the variations in the ozone and the meteorological conditions prevailing in Western Europe, and particularly in Great Britain. On the other hand, Abbot has expressed the view that these variations might be related to the supposed variation of the solar constant. A series of measurements was made during the summer of 1925 by Buisson and Jausseran,‡ at a station where the sky is very clear, in the southern part of the French Alps, near Digne. They found variations in the ozone extending to 15 per cent. but unrelated to local meteorological conditions. That, however, is not necessarily in conflict with the results of Dobson and Harrison, since the Digne station is in the Mediterranean zone, where the meteorological conditions are very different from those of England.

Energy Absorption and Temperature in the Upper Atmosphere.

The amount of energy absorbed by atmospheric ozone from the radiation of the sun is far from being negligible. It would be possible to calculate it exactly if we knew the whole of the spectral energy curve for that radiation, but the extreme ultra-violet region is only known by extrapolation. If we identify the solar spectrum with that of a black body we find that the ozone absorbs 4 per cent. of the incident radiation when the sun is at the zenith.

The effect of this absorption must be to raise perceptibly the temperature of the upper strata of the atmosphere. From meteorological considerations, Lindemann and Dobson have found good reason to suppose that the temperature of the extreme upper atmosphere is much higher than that of the stratosphere, and perhaps comparable with that of the lower strata of temperate regions.

It will be seen that several of the questions raised by the study of atmospheric absorption still await solution, but already the results have considerably exceeded what might have been expected from a subject at first sight very simple. It is probable that further important results will be yielded by it.

* Revue d'Optique, Vol. 2, p. 384 (1923).
† Dobson and Harrison, loc. cit.
‡ Comptes-Rendus de l'Académie des Sciences, Vol. 182, p. 232 (1926).

II.—THE CORROSION PRODUCTS AND MECHANICAL PROPERTIES OF CERTAIN LIGHT ALUMINIUM ALLOYS AS AFFECTED BY ATMOSPHERIC EXPOSURE.

By Professor ERNEST WILSON.

Received May 26, 1926.

(*Communicated by* Prof. E. F. HERROUN.)

ABSTRACT.

The Paper gives an account of experiments which have been made upon the electrical conductivities, the corrosion products and tensile properties of high purity aluminium and certain light aluminium alloys, which have been exposed to London atmosphere for a period of 24 years. The elements concerned are copper, nickel, manganese and zinc in varying amounts up to a few per cent. The variation of electrical conductivity, the growth of the corrosion product and its composition have been studied, and the tensile properties before and after exposure have been compared. Finally, there is a note on the corrosion products of high conductivity copper.

THIS Paper deals with further experiments which have been made on the corrosion products and mechanical properties of certain light aluminium alloys.* All the specimens are in the form of wire 0·126 inch (0·32 cm.) diameter, and have been exposed on the roof of King's College, London. Certain data relating to electrical measurements and loss of metal by corrosion have been taken from a recent Paper in the " Journal " of the Institution of Electrical Engineers.† It is there shown that if $R_0 R_t$ are the electrical resistances at time 0, the commencement of exposure, and time t during exposure, $\rho_0 \rho_t$ the corresponding specific resistances, a_0 the initial volume of unit length of conductor, and b_t the ratio of time t of the weight of metal lost per cm. length of conductor to the specific gravity of the metal, then

$$\frac{R_t}{R_0} = \frac{\rho_t}{\rho_0} \times \frac{a_0}{a_0 - b_t}$$

where the ratio R_t/R_0 is separated into the two terms dealing with the variation of specific resistance and loss of metal respectively. In Fig. 1 curves are given to illustrate the variation of the ratio R_0/R_t with time of exposure t. In Table I are given the chemical analysis, the electrical measurements, and the magnetic susceptibility of the corrosion products. In Table II corrosion products are dealt with from the standpoint of the amount of their variation with time during exposure. Table III

---

* Report of the British Association for the Advancement of Science, 1901, p. 771 ; 1902, p. 734 ; 1903, p. 777 ; 1904, p. 686 ; 1908, p. 827 ; 1911, p. 480 ; 1912, p. 570 ; 1913, p. 606 ; 1915, p. 647 ; also Engineering, 1901, Vol. 72, p. 464 ; Electrician, 1902, Vol. 49, p. 868 ; 1903, Vol. 51, p. 898 ; 1904, Vol. 53, p. 752 ; 1908, Vol. 61, p. 837 ; 1911, Vol. 67, p. 907 ; 1912, Vol.69, p. 945 ; 1915, Vol. 75, p. 886 ; also Journal Inst. Elec. Eng., 1902, Vol. 31, p. 321 ; and Journal of the Royal Society of Arts, 1901-2, Vol. 50, p. 54.
† Journal Inst. of Elec. Eng., Vol. 63, p. 1108 (1925).

Table I.

Group	No. of Specimen	Time in Years *t*	Si	Fe	Cu	Ni	Mn	Zn	Mg	Al	ρ_0 (Sp. res. microhms per cm³ at 15°C) 1901	R_0 (Resistance per cm. microhms at 15°C) 1901	ρ_t (Unexposed Sp. res. microhms per cm³ at 15°C)	ρ_t/ρ_0 (Unexposed)	ρ_t (Exposed Sp. res. microhms per cm³ at 15°C)	R_t (Exposed Resistance per cm. microhms at 15°C)	ρ_t/ρ_0 (Exposed)	$\dfrac{a_0}{a_0-b_t}$	R_t/R_0 Calculated	R_t/R_0 Observed	Gms. per cm. of corrosion remaining on wire	Gms. of metal lost per cm. length of conductor	K_v Unexposed 1917	K_v Exposed 1926	K_v Exposed 1926	K_m	Sp. gravity Corrosion Product
I	25	0	0·14	0·31	…	…	…	…	…	99·55	2·773	34·39	…	…	…	…	…	…	…	…	…	…	4·17	…	…	…	…
I	25	8	0·14	0·31	…	…	…	…	…	99·55	2·773	34·39	…	…	2·943	41·12	1·061	1·127	1·193	1·150	0·01383	0·0247	…	…	3·59	105	1·1
I	25	23	0·14	0·31	…	…	…	…	…	99·55	2·773	34·39	2·773	1·00	3·032	43·67	1·093	1·160	1·269	1·240	0·0112	0·0302	3·73	3·47	…	161	…
II	4	24	0·38	0·25	0·16	…	…	…	…	99·21	2·88	36·38	2·893	1·005	3·187	42·20	1·107	1·048	1·160	1·140	0·0035	0·0100	…	…	…	…	…
II	13	24	0·38	0·25	1·58	…	…	…	…	97·79	3·30	41·56	…	…	4·113	54·09	1·246	1·044	1·301	1·280	0·0030	0·0092	…	…	1·93	…	…
II	15	24	0·40	0·40	2·61	…	…	…	…	96·59	3·34	…	…	…	…	…	…	…	…	…	…	…	2·32	…	…	…	…
III	7	24	0·37	0·25	0·05	0·75	…	…	…	98·58	3·05	38·30	…	…	3·327	42·83	1·091	1·025	1·119	1·110	0·0030	0·0054	…	…	…	…	…
III	8	24	0·35	0·29	0·09	1·19	…	…	…	98·08	3·24	40·76	3·161	·9757	3·634	45·68	1·121	1·017	1·140	1·130	0·0036	0·0036	…	…	…	…	…
III	21	24	0·39	2·57	0·10	1·39	…	…	…	95·55	3·195	40·00	…	…	3·454	44·51	1·081	1·030	1·113	1·106	0·0028	0·0063	…	…	5·95	…	…
III	22	24	0·37	0·43	1·08	1·29	…	…	…	96·83	3·28	41·44	3·346	·9694	3·797	48·97	1·144	1·030	1·183	1·130	0·0020	0·0064	…	…	…	…	…
IV	9	24	0·31	0·35	0·03	…	0·35	…	…	98·96	3·30	41·64	…	…	3·642	47·25	1·104	1·019	1·124	1·136	0·0028	0·0060	…	…	…	…	…
IV	23	24	0·44	0·56	0·09	…	1·78	…	…	97·13	3·35	42·06	…	…	3·683	48·60	1·100	1·051	1·156	1·160	0·0037	0·0106	…	2·28	…	161	…
IV	26	8	…	…	3·5 to 5·5	…	0·5 to 0·8	…	0·5	…	5·35 (1911)	64·95 (1911)	5·106	·9543	5·929	74·71	1·109	1·038	1·150	1·153	0·01109	0·0083	8·26	0·86	…	…	…
V	5	24	0·43	0·39	0·09	…	…	2·04	…	97·05	3·07	38·47	…	…	3·368	43·87	1·097	1·040	1·141	1·127	0·0022	0·0084	…	…	…	…	…
VI	Hard-drawn Copper	4	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	12·8	150	…
VI	Annealed Copper	4	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	…	4·27	86	1·85

gives the data derived from the tests made of the mechanical properties of representative alloys. Owing to the fact that about half the alloys, numbering 26, were annealed before exposure, the choice of specimens was restricted. It was, however,

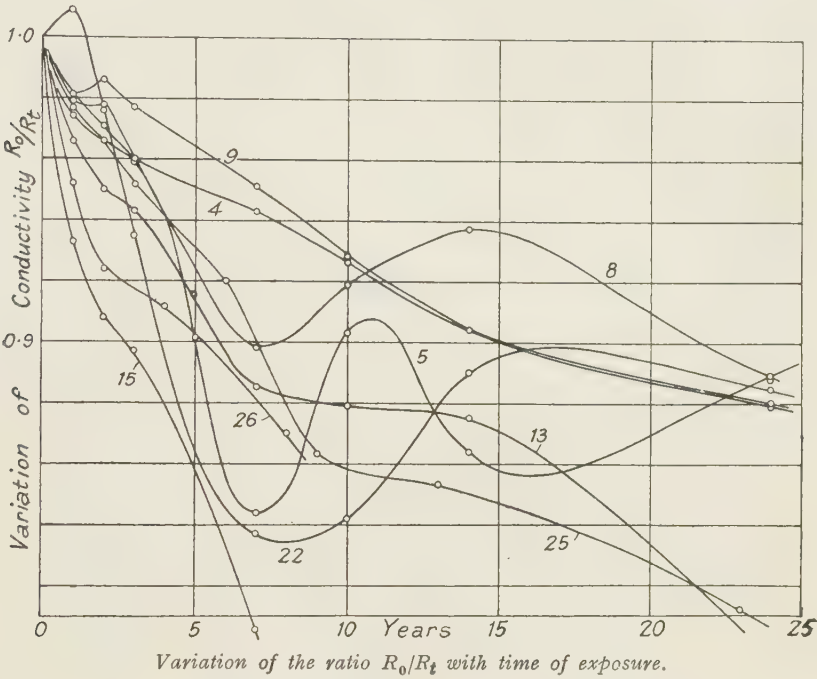*Variation of the ratio R_0/R_t with time of exposure.*

FIG. 1.

possible to test unannealed specimens from each of the groups dealing respectively with alloys of copper, nickel, manganese and zinc, in addition to the high purity specimen No. 25.

TABLE II.

Group.	No.	Exposure in years.	Specific Resistance. Micr-ohms/cm.³ 15°C.	Radius of Metal.	Radial Thickness of Corrosion Product.	Volume of Corrosion per cm. of Conductor.	Gms/cm. of Corrosion remaining on Wire.	Apparent Density of Corrosion Product	Density measured.	Gms. of Metal Lost per cm. of Conductor.	Superficial Area per cm. of Conductor.	Gms. of Metal Lost per sq. cm. of Superficial Area.
				cm.	cm.	cm.³					cm.²	
I	25	0	2·773	0·1603	...	...	...	...	...	...	1·007	...
		8	2·943	0·1510	0·0137	0·01358	0·01383	1·018	1·11	0·0247	0·978	0·0253
		23	3·032	0·1488	0·0137	0·01339	0·0112	0·836	...	0·0302	0·974	0·0310
IV	26	0	5·350	0·162	...	...	...	...	...	...	1·018	...
		2	5·650	0·161	0·0063	0·006496	0·00800	1·23	...	0·00546	1·012	0·00553
		8	5·930	0·159	0·0058	0·005898	0·01109	1·88	...	0·00830	0·999	0·00829

TABLE III.

Group	No.	Time of Exposure (Years)	Diameter (Ins.)	Area (Ins.²)	Elastic Limit Tons per sq. in. 1901	Elastic Limit Tons per sq. in. 1926	Breaking Load Tons per sq. in. 1901	Breaking Load Tons per sq. in. 1926	Modulus Tons per sq. in. 1901	Modulus Tons per sq. in. 1926	Ratio Elastic Limit/Breaking Load Per cent. 1901	Ratio Elastic Limit/Breaking Load Per cent. 1926	Elongation Per cent. Including Fracture on 35 cms. 1901	Including Fracture on 35 cms. 1926	Excluding Fracture 1901	Excluding Fracture 1926	Local Extension at Fracture per cent. of Diameter 1926
I	25	0	0·126	0·0125	8·65	5·35 / 5·30	12·6	11·4 / 11·45	3,800	3,750	67·5	47	1·86	1·6	...	1·0	70
		8	0·119	0·0111	...	4·75	...	11·0	...	3,900	...	43	...	0·95	...	0·55	45
		23	0·115	0·0104	...	5·00	...	11·4	...	3,950	...	44	...	0·9	...	0·5	45
II	4	24	0·120	0·0113	7·88	5·6	11·31	10·3	3,670	3,900	69	54	3·4	2·0	...	1·50	60
	13	24	0·1207	0·0114	14·3	3·8	17·9	7·8	3,690	4,200	83	47	3·7	...	...	3·0	...
III	8	24	0·1238	0·0120	10·4	5·7	14·9	12·8	3,020	4,050	70	44	4·0	0·75	2·5	0·5	27·5
IV	9	24	0·116	0·0106	9·85	5·9	13·4	13·0	3,920	4,200	73	45	2·0	1·6	1·5	1·0	70
	26	8	0·1243	0·0122	...	7 to 13	30(1911)	21·0	...	3,800	...	33 to 62	12 to 15 (1911)	0	...	0	0
V	5	24	0·119	0·0111	9·13	5·2	11·5	10·4	4,180	4,250	80	50	3·2	1·0	2·4	Less than 1·0	40

I. High Purity Aluminium.

Aluminium for electrical purposes has a purity of 99·5 per cent. or over, and from this standpoint specimen 25 is of special interest. Curve 25, Fig. 1, shows that conductivity diminishes at a greater rate during the first 10 years of exposure than subsequently, and the diminution of conductivity after 23 years' exposure is more largely due to loss of metal than to increase in specific resistance (Table I). The loss of metal in gms. per sq. cm. of superficial area, and also the variation in specific resistance are given in Table II, and illustrated by curves in Fig. 2. Neither of these curves is parabolic, but the latter is more nearly so than the former. Examination shows that the radial thickness of corrosion product remaining on the conductor is substantially the same at eight and twenty-three years' exposure, and this is possibly due to the diminished rate of production of corrosion as time goes on, accompanied by loss of corrosion due to exposure. The values of the apparent density in Table II, as determined by the method of measuring diameters, are neces-

No. 25. Aluminium Wire. 99·55 per cent purity. 0·32 cm. diameter
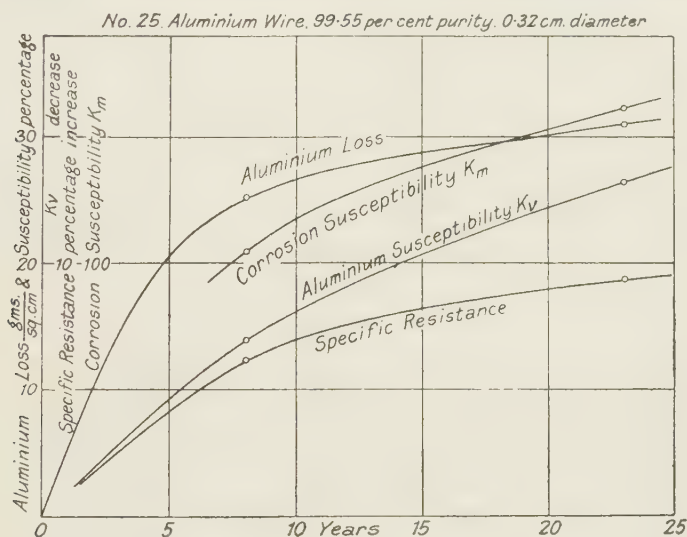
Fig. 2.

sarily approximate, and are somewhat lower than the separately determined value at eight years' exposure. Examination of the corroded portion, kindly made by Prof. E. F. Herroun, F.I.C., and given in the previous Paper, showed that it consisted mainly of alumina and metallic aluminium. It also contained sulphate in appreciable quantity, and a trace of chloride, also traces of iron, probably derived in part from the emery paper used for its removal, but no zinc or nickel. There was, therefore, a question as to the origin of the iron. A sufficient quantity for further test was removed with the sharp edge of a piece of glass, and further examination shows that there is much more than the 0·31 per cent. of iron contained in the aluminium itself. To test this further, measurements of magnetic susceptibility have been made, and these are given in Table I and illustrated by curves in Fig. 1. The mass-susceptibility k_m was found to be greater after 23 years' exposure than after 8 years. Assuming the density to have an approximate value equal to unity,

c2

the volume and mass-susceptibilities k_v k_m have about equal values, and this enables a direct comparison to be made with the susceptibility of the aluminium itself. The first magnetic tests of these alloys were made on the unexposed specimens in 1917.* The values given in Table I show that as time progresses the magnetic susceptibility of the aluminium itself diminishes in value. Also the susceptibility of the corrosion product is very large in comparison with that of the aluminium itself. The conclusion is that the iron present in the corrosion product must have come from an outside source.

In the mechanical tests, the results of which are given in Table III, the values are those obtained on a first loading. The distance between the grips was 9 inches, and the extension was measured between marked points 3 inches apart on the central portion of the wire. The accuracy obtainable with the extensometer used was 0·0001 inch on 3 inches. The tests bring out one important feature, in that the 1926 values of the breaking load and the elastic limit are substantially the same in the unexposed and exposed specimens. The reduction on the 1901 value of the breaking load amounts in 23 years to about 9 per cent., and that of the elastic limit is 60 per cent. As regards the 1926 elongation values, it will be noted that a very considerable reduction occurs as between the unexposed and exposed specimens. On the other hand, the elongation including fracture obtained in 1901 has only diminished 14 per cent. The break was normal in character, with the usual drawing down.

A comparison of the electrical and mechanical properties of specimen No. 25 with those of present-day wires is given in the recent Institution of Electrical Engineers' Paper.†

II. Copper.

It is interesting to compare the curves 4, 13 and 15 in Fig. 1 as regards the variation in electrical conductivity. Alloy 4 (curve 4), containing 0·16 per cent. of copper, diminishes in conductivity at a fairly steady rate. Table I shows that its increase in electrical resistance is largely due to increase in specific resistance, and the loss of metal is small. The presence of the copper has very largely reduced corrosion, and the final resistance R_t is smaller than in the case of alloy 25. Both the breaking load and the elastic limit are smaller than in No. 25, and the elongation is considerably larger.

Alloy 13 was annealed before exposure, so that the 1926 figures cannot properly be compared with those of No. 4. The tests made in 1901 before annealing showed that the tensile strength was considerably increased by the larger proportion of copper, and this was accompanied by an increase in specific resistance. Comparing curves 13 and 25 in Fig. 1, there is a similarity, but the increase in specific resistance in No. 13 almost wholly accounts for the fall in conductivity. It was not possible in No. 13 to estimate the elongation including fracture. The break shows a flaky and brittle material at the surface of the wire, thereby preventing reduction of section at the fracture, which invariably takes place in the grips. The core appears to be very ductile and possibly strong, but the outer material cracks long before the breaking point of the centre portion is reached. When the percentage of copper

---

* Proc. Roy. Soc., A, Vol. 96, p. 429 (1920).
† Ibid.

reaches 2·61, as in alloy No. 15, a most unsatisfactory material is produced. Curve 15, Fig. 1, shows that the conductivity falls rapidly during exposure, and, as was pointed out in 1911,* almost complete disintegration had then taken place.

III. NICKEL.

One remarkable feature of the nickel alloys is the way in which electrical conductivity varies during exposure. Reference should be made to the curves 8 and 22, Fig. 1, in this connexion. From the information given in Table I it will be gathered that the final increase in resistance is almost wholly due to increase in specific resistance ; whereas specific resistance is reduced in value in the case of the unexposed specimens tested.

Alloy No. 8 was not annealed before exposure, and has been tested for its mechanical properties. The breaking load before exposure in 1901 was fairly high, and it has been well maintained, and the total loss of metal by corrosion has the relatively small value of 0·0036 gms. per cm. length of conductor. The elastic limit and percentage elongation have suffered considerable reduction.

Specimens 21, 22 were annealed before exposure, but they have lost very little by corrosion, and are in excellent condition. They had the highest tensile strength of any of the series before annealing. No. 22 is specially interesting, in that its copper-nickel content, treated as a group, has proportions (Cu 45·6, Ni 54·4) more nearly approaching those of the well-known alloy constantan. No. 22 has a relatively low temperature coefficient (0·00173), which is about half that of the other alloys. Its specific resistance is relatively high, as also its coefficient of linear expansion (0·0000252), thereby pointing to a possible direct influence of the Cu-Ni proportions.

Having regard to the great variation of the ratio R_0/R_t in the nickel alloys of aluminium, it was thought that if specimens of No. 25 and No. 8 were submitted to alternate heating and cooling they might vary resistance after the manner of the curves 25 and 8 in Fig. 1. For this purpose a hydraulic motor, controlled by a clock, was used to raise and lower the two specimens from a bath of oil maintained at a temperature of 80°C. The time intervals were $7\frac{1}{2}$ minutes in the oil bath and $7\frac{1}{2}$ minutes in air. The conductors were tested at intervals for electrical resistance. In the case of the high purity specimen 25, the resistance continuously fell from its initial value, but the nickel alloy behaved after the manner of curve 8, Fig. 1. The number of cycles required to produce a fairly constant resistance was 5,122. In Fig. 3, curve 1 shows the variation of specific resistance in alloy 8 during exposure, and curve 2 that of the same alloy during the above heating and cooling experiment.

IV. MANGANESE.

Alloy 26 is a specimen of duralumin first exposed in 1911. Before exposure the breaking load was stated to be 30 tons per sq. inch and the elongation 12 to 15 per cent. It was pointed out in the Reports of the British Association (1913 and 1915) that it becomes brittle on exposure. The specimen was exposed for 8 years, and since then has been loosely coiled up in the laboratory. The breaking load is now 21 tons per sq. inch, and the material is now extremely brittle, and no

---

* The Electrician, Vol. 67, p. 907 (1911).

elongation was measurable. At fracture there is an outside annulus of darker material than at the centre, and there is no contraction at all.

It is shown in Table I that an unexposed specimen of duralumin (26) has diminished in specific resistance; whereas the exposed specimen has largely increased, the ratio ρ_t/ρ_0 being 1·109. The loss of metal per sq. cm. of superficial area is about one-third that of alloy 25, the period of exposure being 8 years in each case. The radial thickness of corrosion remaining is practically the same at 2 and 8 years (Table II), and this was also the case with specimen 25. Its temperature coefficient (0·00173) of electrical resistance is identical with that of specimen 22. An interesting comparison is that between curves 15 and 26 in Fig. 1. The former is a copper alloy containing 2·61 per cent. of copper, and it is possible that the high percentage of copper in the duralumin is responsible for the rapid fall in conductivity.

The magnetic susceptibility of the duralumin in the exposed condition is very much smaller than that of the high purity aluminium. This is remarkable, as man-

Variation of electrical resistance with cyclical changes of temperature.
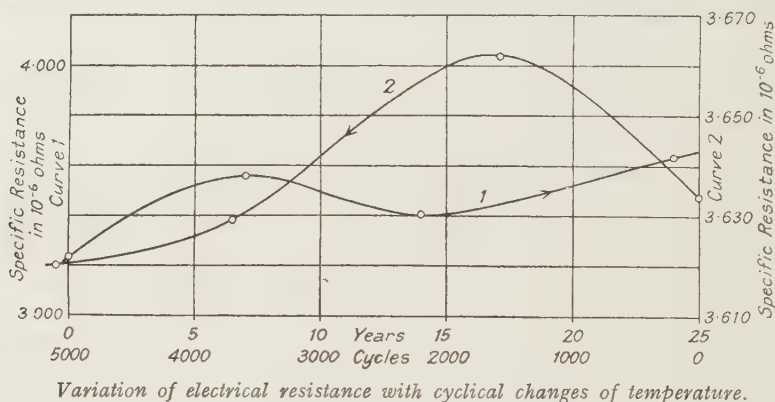
Fig. 3.

ganese in the presence of copper and aluminium might be expected to enhance susceptibility. Copper alone (alloy 15) gives a high result relatively to pure aluminium,* and manganese in the presence of small copper content in alloy 23 also gives a high result. It would seem that the low susceptibility in No. 26 is either associated with magnesium present or duration of exposure (*see* No. 23). The susceptibility of the corrosion product of duralumin is identical with that of the 23 year exposed high purity aluminium 25.

No. 9 is another manganese alloy, not containing magnesium, which was not annealed before exposure, and which has been tested for mechanical properties. It will be seen in Table III that the breaking load during 24 years' exposure has been well maintained, and the elongation, though diminished, is equal to that in the unexposed No. 25. Curve 9, Fig. 1, shows that the conductivity gradually falls, and this is due almost wholly to increase in specific resistance. Alloy 23 is very similar in its behaviour. The magnetic susceptibility of the exposed metal, though not so small as in duralumin, is very much smaller than in the unexposed specimen.

---

* See Landolt-Börnstein, and Kaye and Laby Tables.

V. Zinc.

Specimen 5, containing about 2 per cent. of zinc, shows a variable conductivity, as in the case of the nickel alloys. The loss of metal is small, and about equal to that in the duralumin. As the specimen was unannealed, it was tested for its mechanical properties. The ultimate strength has dropped from 11·5 to 10·4 tons per sq. inch in 24 years, and the elongation has fallen considerably.

VI. High Conductivity Copper.

The corrosion products on annealed and hard-drawn copper have been kindly examined by Prof. E. F. Herroun, F.I.C. In the annealed specimen the aqueous solution from the powder (cold) contained quite an appreciable amount of $Cu SO_4$, but no soluble iron. The residue was partly soluble in HCl, giving both $Cu_2 Cl_2$ from cuprous oxide and $Cu Cl_2$ from cupric oxide. It also contained a quite definite amount of iron and traces of alumina, but rather less of the latter than in the case of the hard-drawn specimen. There was a fair amount of copper sulphide insoluble in HCl, and also carbon. After 4 years' exposure the volume-susceptibility had the value $4·27 \times 10^{-6}$, and the mass-susceptibility of the corroded portion was 86×10^{-6}. The specific gravity of the corrosion product was found to be 1·85.

The deposit from the hard-drawn wire contained copper sulphide, oxide and basic sulphate. It also contained carbon and iron (probably as an oxide) in considerable amount ; also alumina, probably from neighbouring wires. After 4 years' exposure the volume-susceptibility of the copper was $12·8 \times 10^{-6}$, and the mass-susceptibility of the corrosion 150×10^{-6}. The mechanical properties of these conductors have not been examined, and the results of the electrical tests were given in the recent Institution of Electrical Engineers' Paper.*

In conclusion, the author wishes to cordially acknowledge the help he has received from Mr. C. M. White, B.Sc., who carried out the mechanical tests.

DISCUSSION.

Mr. J. C. Hudson : I should like to express appreciation, for Dr. W. H. J. Vernon and myself, of your kind invitation to contribute to the discussion. Dr. Vernon, who greatly regrets his unavoidable absence this evening, has now been engaged in an investigation on atmospheric corrosion for the British Non-Ferrous Metals Research Association for several years. The study of the more fundamental aspects of the problem has left him very little time for field tests, and I was therefore appointed some eighteen months ago to extend the investigation to outdoor conditions of exposure. Unfortunately, the sensitive physical methods (increase in weight and loss in reflectivity) used by Dr. Vernon in his experiments on tarnishing in indoor atmospheres† are not applicable outdoors, beyond the early stages of attack, and ultimately we decided to use the change in resistance of a wire specimen as a quantitative index of corrosion. Our work in this field is thus very similar to that of Professor Wilson, and we are extremely interested in his results.

We have, however, developed our research along slightly different lines. Professor Wilson's work is perhaps more intimately concerned with the mechanical and electrical properties of the materials than with corrosion proper ; in consequence he has been led to use wires of dimensions that would be far too unwieldy for our purpose, as we wish to arrange for exposure in several localities and to obtain results in a much shorter time.

* Ibid.
† W. H. J. Vernon, Trans. Far. Soc., 19, 839 (1924) ; J. C. S., 2,273 (1926).

The relative increase $\dfrac{dR}{R}$ in the resistance of a circular wire of radius r, due to the removal of a thin film of metal of thickness dt is given by

$$-\frac{dR}{R} = 2\frac{dr}{r}$$

It follows that if dr, the depth of the metal corroded, is independent of the dimensions of the wire, the observed change in resistance is inversely proportional to the radius, and the time necessary to bring about a given change can be considerably reduced by the use of thin wire. We are therefore using much smaller specimens than Professor Wilson, and the gain in portability, ease of manipulation and time of exposure will probably compensate for the loss of the mechanical tests.

The equation given above is based on the assumption that the specific resistivity of the material remains constant, and we therefore view with some concern the fact that Professor Wilson reports variations in this property. It is probable, however, that these irregularities, particularly those shown by alloys 5, 8 and 22, might have been prevented by suitable treatment of the materials before exposure, since it is known, for instance, that changes in internal structure may be very greatly reduced by annealing. Thus Matthiessen,[*] and later Fitzpatrick,[†] found that the resistance of annealed wires did not vary over many years. The unsatisfactory behaviour of nickel silver has been overcome by modern metallurgical methods,[‡] and Professor Wilson's own observation that alloys 8 and 25 reached a constant specific resistance after 5,000 cycles of heating to 80°C. and cooling is further evidence of the efficacy of annealing. Finally, I have found that six hours' annealing in hydrogen at 200°C. is sufficient to bring specimens of copper and brass to a constant resistance ; that is, no further resistance change is observed if the annealing is repeated.

Dr. Vernon has asked me to mention that his own work on very pure materials confirms Professor Wilson's view that the iron in the corrosion product is derived from outside sources. There is also no doubt of the high sulphate content of the corrosion product ; in some cases the sulphate crystals become visible after a few months' exposure. The fact that the monthly SO_3 deposit varies from 6 tons/Km^2 in London to 0·2 tons/Km^2 at Malvern illustrates the force of Professor Wilson's remark that corrosion may vary from one district to another.

In conclusion, Dr. Vernon joins me in expressing our great appreciation of Professor Wilson's experiments, which constitute pioneer work in this field.

Mr. EDGAR T. PAINTON (The British Aluminium Co., Ltd.) : The problems which Prof. Wilson has been studying are of the utmost practical importance, for aluminium conductors are now employed very extensively for overhead transmission lines, and indeed, at the present time are employed for the majority of the longest and highest voltage lines of the world. During the time Prof. Wilson's specimens have been exposed, we, who are engaged in the industry, have been studying from the practical point of view the same phenomena which he had set out to investigate, and it is interesting to compare the deductions to be drawn from his investigations with the facts we have proved from our practical experience.

Prof. Wilson's tests are made on both pure aluminium specimens and on aluminium alloy specimens, and it will be seen from Fig. 1 that as regards resistance to corrosion, the pure specimens are not markedly superior to the alloys and in some instances decidedly inferior. This is not in accordance with our experience and we have found that beyond all shadow of doubt, pure aluminium is capable of better service than alloys—at least than such alloys as Prof. Wilson has investigated. Confirmation is afforded by the fact that while, 25 years ago, aluminium alloy wires were sometimes advocated, at the present time overhead lines are practically invariably of pure aluminium. (In passing it may be remarked that recent discoveries of special non-corrosive alloys may possibly lead to an increased use of aluminium alloy conductors in the future, but this has no bearing on the present point.)

An explanation for this discrepancy can be sought only in the particular specimen of pure aluminium which Prof. Wilson employed, and without going into the subject very deeply it can be stated at once that Specimen 25 though probably typical of good quality aluminium 25 years ago, is not typical of the metal now used for electrical purposes.

* Matthiessen and Bose, Phil. Trans. A, **152**, 1 (1862).

† Fitzpatrick, British Association Electrical Reports, p. 502 (1894).

‡ W. A. Price, "The Measurement of Electrical Resistance" (Clarendon Press).

The point is particularly interesting in that the electrical conductivity of Prof. Wilson's sample was especially good, and in 1901 the wire would have been regarded as eminently satisfactory for overhead line purposes. Our present-day knowledge leads us to surmise that the particular factors which give specimen 25 its low specific resistance are the very factors which render it less capable of resisting corrosive influences.

AUTHOR'S reply : I wish to express my thanks to Dr. W. H. J. Vernon and Mr. J. C. Hudson for their very kind remarks. I appreciate the valuable additions which Dr. Vernon has made to our knowledge of the difficult subject of corrosion, and I look forward with interest to the results of Mr. Hudson's work. His wires are smaller in diameter than mine, and it becomes a question as to how far the depth of metal corroded is dependent upon diameter. Moisture condenses less readily on a fine wire, and this conceivably may play an important part. As regards the variation of specific resistance exhibited by curve 2, Fig. 3, it is only stated that the number of cyclical changes in temperature produced a fairly constant resistance, not that the latter is equivalent to the value obtained before exposure. Wires which have been carefully annealed, and used, for example, in resistance boxes, retain a wonderfully constant resistance ; but in exposed conditions the result may be different. For example, alloy 22 was carefully annealed before exposure at a temperature of 436°C. for half an hour and cooling in air, and it exhibited great fluctuations in specific resistance. The ratio of the specific resistances ρ_t/ρ_0 had the value 1·144 after 24 years' exposure. Alloy 21 is another example, and there are others. As copper melts at about 1,084°C., an annealing temperature of 200°C. appears low, and there is the possible influence of occluded hydrogen. It would be interesting to raise the temperature of Mr. Hudson's copper conductors to, say, 800°C., in an evacuated quartz furnace, as a check upon the value and constancy of specific resistance. I am very pleased to learn that Dr. Vernon, working with very pure specimens, has found sulphate and iron in considerable quantities.

I desire to thank Mr. Painton for his remarks which I feel sure will be read with interest by Fellows of the Society.

III.—THE DISTRIBUTION OF INTENSITY IN A POSITIVE RAY
SPECTRAL LINE.—PART II.

By M. C. Johnson, *M.A., M.Sc.*

Received July 29, 1926.

ABSTRACT.

The study of optical spectra of positive rays is continued with the type of tube and Merton
wedge described previously. The direction of observation is here longitudinal, in order to isolate
the Doppler effect in the " moving " spectrum : accordingly a six-prism spectrograph is sub-
stituted for the échelon used with a narrower line in Part I. The results are added to those of
Stark, Paschen, Wilsar and Krefft on the same spectrum, and the uncertainties in identifying
atomic and molecular carriers are analysed. The distribution of velocity among the particles
contributing to the " moving " spectrum is compared with the distribution of velocity in positive
rays measured by the electromagnetic method and with some investigations of Retschinsky and
Döpel. The appearance of the many-lined spectrum of hydrogen in the positive rays, and the
ratio of intensity of the " moving " and " resting " spectra are also considered. The inverse
square law of probability of electron capture, and some consequences of the work of Wien and
Rüchardt, are the most likely controlling factors in the several phenomena.

I.   INTRODUCTION.

WHEN a beam of positive rays streams through a perforated cathode, it gives
rise to two spectral lines for each radiation of the gas in the tube. One
line is emitted by the positive rays, and is known as the " moving spectrum " ; the
other is excited by the rays when they strike the stationary gas already behind the
cathode. This is known (following Stark) as the " resting spectrum." In a previous
Paper* it was found possible, by the high resolving power of an échelon and the use
of a Merton wedge, to distinguish these two lines, even when superposed by the axis
of the optical train being set perpendicular to the direction of the positive rays.
In the present Paper the distribution of intensity in the moving line itself is studied
by the Merton wedge ; accordingly the axis of the optical train was placed parallel to
the direction of the positive rays. The full Doppler displacement of the moving line
in this direction is so large that a six-prism spectrograph was substituted for the
échelon used in Part I. Various analyses of the moving line have been made by
other workers, chiefly Wien and his pupils, and Stark and Paschen. It is believed
that new aspects of the problem of the carriers of the moving spectrum and its
conditions of excitation can be investigated by the present method, and the possibility
of understanding the conflicting results of previous investigators increased.

II.   EXPERIMENTAL DETAIL.

The discharge tube used was of the type illustrated in Part I, consisting of two
glass cylinders waxed on to opposite sides of a central plate which contained the
cathodes. In place of the metal end to the positive ray chamber, which in the
previous experiments contained the third electrode for the Stark effect, a glass plate

---

* Proc. Phys. Soc., Vol. 38, Part 4, p. 324 (1926).   Referred to as Part I.

was waxed to the end of the chamber and the back of the cathode viewed longitudinally. The gas pressure was uniform in both chambers, and controlled by pumps. and hydrogen reservoir as before. Two cathodes used are seen in Fig. 1.

For details of technique reference must be made to Part I, including discussion of the relation of Balmer to many-lined spectrum intensity in hydrogen, the thermostatic and mechanical stability of the apparatus, and the method and limits of the Merton wedge measurements. In the present case the ammonia-stained panchromatic plates used for H_α were discarded, as the greater dispersion of the prisms at H_β was utilised. Hence, Imperial Eclipse plates were used without any hypersensitising. The chief technical requirement beyond those of Part I was constancy of gas pressure and voltage and current relations during exposures up to ten hours. It was found that after the tube had been running for about 40 hours, pressure

(a) (b)

W = Water cooling
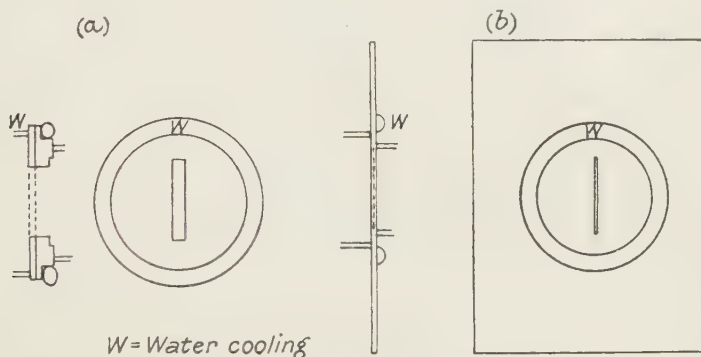
FIG. 1.

increases due to gassing of surfaces were negligible. After several weeks the opposite effect of hardening during discharge began to appear. The best photographs were taken in the intermediate periods, in which the length of the cathode dark space could be guaranteed within one millimetre throughout several hours. This was important, since it was found in Part I that fresh introduction of gas vitiates temporarily the Balmer spectrum. The potential between the ends of the tube was measured by an electrostatic voltmeter. According to Aston,* at low voltages this potential measures the fall in the cathode dark space, and is, therefore, the maximum through which the positive ions can fall. In all cases the 16-in. spark coil was used, as before, driven on half voltage.

III. CALIBRATION OF SPECTROGRAMS.

The spectroscope used was of the Evershed pattern designed for solar prominence work. It consists of two groups of prisms, each comprising a direct vision combination of three ; between the two groups is an adjustable mirror, which allows any spectral range of about 300 A.U. wide to be brought on to the plate of an improvised camera. For calibration purposes, advantage was taken of the map of the many-lined hydrogen spectrum published by Merton,† and the list of lines in that spectrum

* "Isotopes," p. 25.
† Proc. Roy. Soc., 96, 382 (1920).

published by Merton and Barratt.* By photographing an old hydrogen tube in which the primary spectrum had decayed, every one of the 17 lines between $\lambda4860$ and $\lambda4800$ in Merton's photograph could be recognised.   The following stronger lines were used to plot a dispersion curve :—

$$4873\cdot05$$
$$4869\cdot42$$
$$4867\cdot05$$
$$4849\cdot34$$
$$4843\cdot35$$
$$4838\cdot25$$
$$4832\cdot79$$
$$4822\cdot96$$
$$4807\cdot33$$
$$4797\cdot76$$

From this curve the dispersion at H_β was found to be 0 039 A.U. per division of the Watson micrometer used.

IV. MEASUREMENTS OF DISPLACED H_β.

Fig. 2 shows the distribution of intensity in three examples with cathode (a), the gas pressure, and consequently the fall of potential, being varied.   The " moving " line is in each case quite separated from the " resting " line.   The steepness and sharpness of the latter as measured by a micrometer on the wedge images indicates the advantages of this method.   Except for the measurements of Koch by photoelectric microphotometry, and the thermoelectric microphotometer of Moll, the alternative to Merton's wedge is a visual estimation by compensation of degree of blackening in an image.   The difficulty of distinguishing between very sharp rises of intensity by those visual estimations in a Hartmann microphotometer has probably been responsible for obscuring in most previous work the tendency to asymmetry of the moving line.   This asymmetry is evident in each example of Figs. 2 and 3, though in order to take a negative of such a faint source, capable of showing detail of the fainter parts if printed and enlarged, the centre of the image is in danger of over-exposure to the point of blurring this feature.

The sharpest and steepest limit to visibility of the moving line is, in each case, on the side nearest to the resting line ; the rise to maximum is hardly distinguishable in steepness from that of the latter.   On the contrary, the fall from maximum on the side furthest away from the resting line is more gradual and diffuse.   On account of this diffuseness on the violet side, all efforts to do more than assert an asymmetry cannot be relied on ; its existence is beyond doubt, but its shape cannot be identified as a curve, and differences in the falling part of the intensity distribution have not been isolated from the error which, on this edge of the image, is several times as great as on the inner edge.   A better elimination of error in wedge measurements has been effected by Merton,† by enlarging the image through a ruled screen and counting the dots in the grain.   Unfortunately, the part of the positive ray line which is as intense as Merton's lines is the red side, which is that least susceptible to error, while the diffuse edge ends too faintly to be enlarged on a scale suited to the remainder

---

* Phil. Trans., 222, 369 (1922).
† Phil. Trans., 216, 465 (1916).

1.—H_β IN POSITIVE RAYS. "MOVING" AND "RESTING" LINES. WEDGE IMAGE.
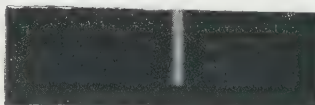
2.—H_β IN POSITIVE RAYS. "MOVING" AND "RESTING" LINES.
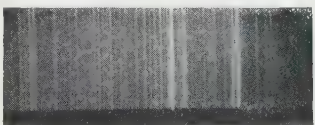
3.—COMPARISON SPECTRUM OF H_β REGION IN ORDINARY TUBE.
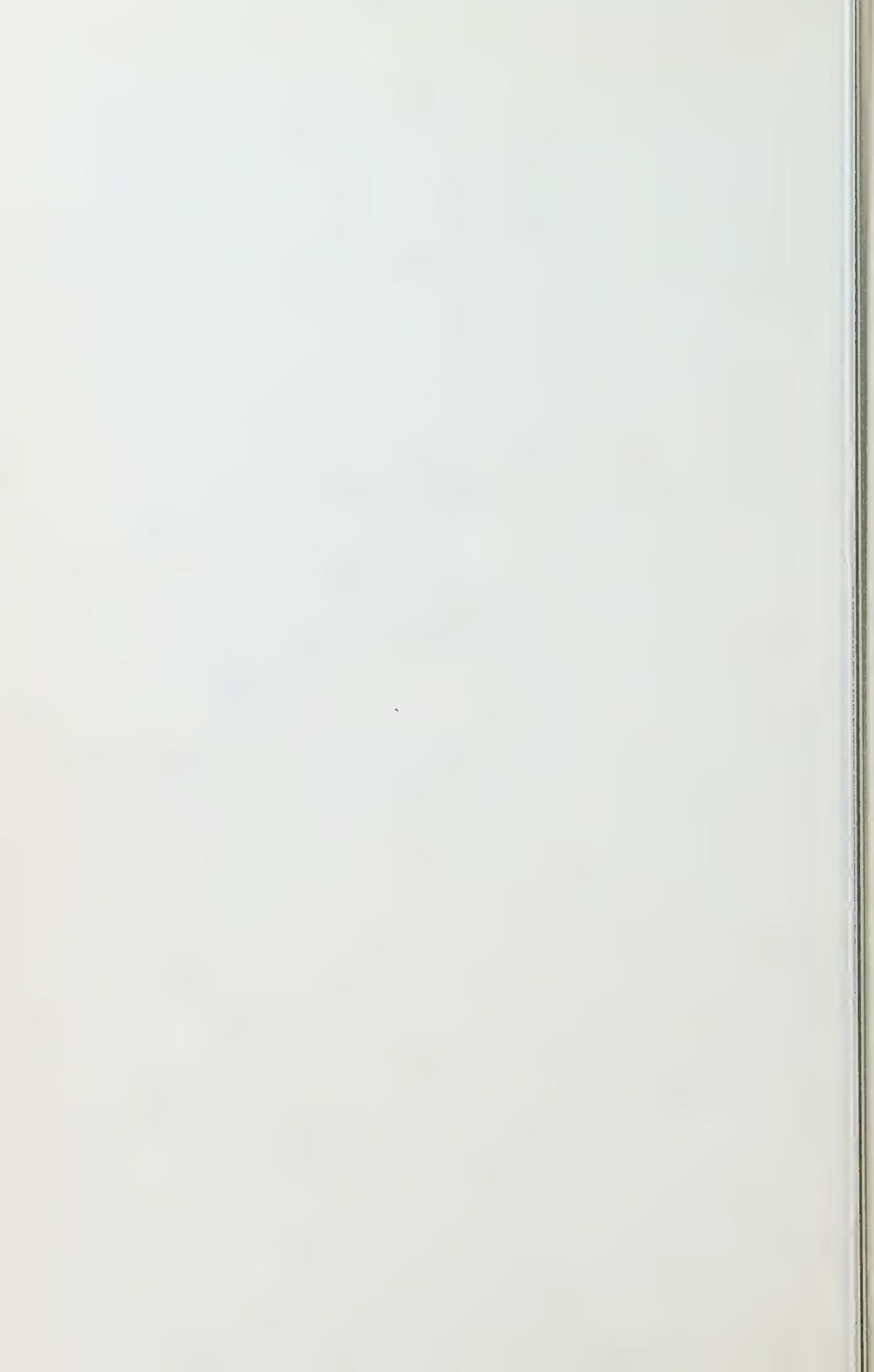
of the line. In the graphs the regions on which it is most difficult to set a micrometer wire are dotted ; this indicates the relative error expected, and also shows up the asymmetry by contrast of sharp and diffuse edges.

Fig. 3 shows spectrograms in which attempts were made to alter the intensity distribution by varying the velocity distribution in the positive rays. Plate 12 (*see* Fig. 3) was made with cathode (*b*). According to Aston,* and Gehrcke and Reichenheim,† the distribution of the rays is sensitive to changes in the shape of the cathode. Plate 10 (*see* Fig. 3) was made with a condensed discharge. The

1400 volts   1800 volts   2400 volts
1·8 cm. dark space   2·9 cm. space   4·1 cm space
4 hours   5 hours   2½ hours
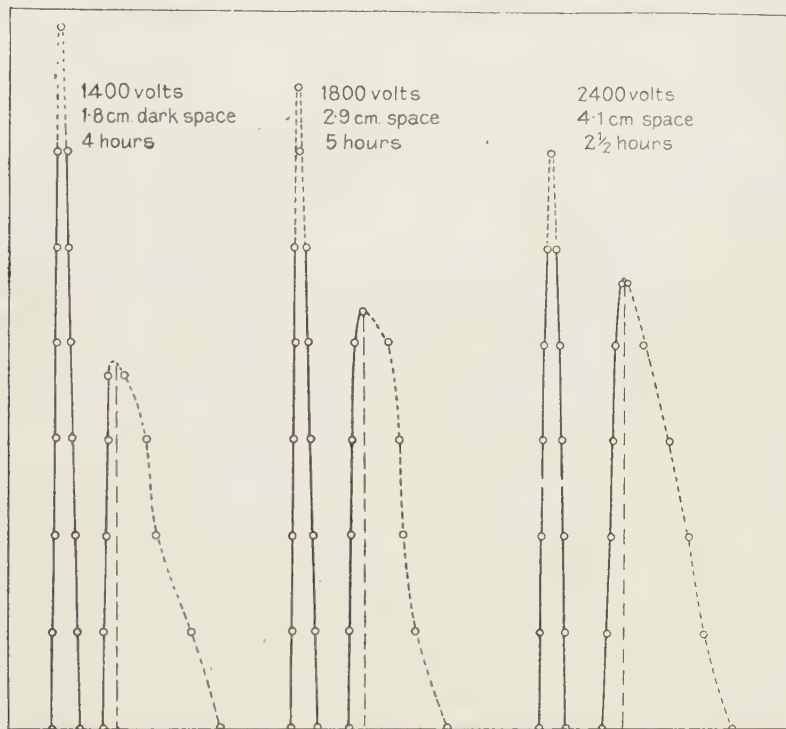
FIG. 2.

significance of this will be discussed later in connexion with the actual nature of the velocity distribution. In both of these cases the asymmetry of the moving line still appears. In view of the maximum error being on the violet side, it is not thought advisable to attach any meaning at this stage to the apparent slight lessening of the asymmetry in Plate 12 (*see* Fig. 3).

V. THE MANY-LINED SPECTRUM.

The many-lined or secondary spectrum of hydrogen is always fainter than the Balmer lines in the positive rays, as discussed in Part I. Nevertheless, measurement of it is important here for two reasons : Firstly, it is necessary to make sure that the

* Proc. Camb. Phil. Soc., 19, 321 (1919).
† Wien : Kanalstrahlen, p. 237 (1923).

observed structure of the moving Balmer line is not complicated by the superposed presence of one of the secondary lines—a precaution I cannot find dealt with in the previous work on this problem. Secondly, Rau* is the only investigator out of many who has notified a Doppler effect in the secondary spectrum of hydrogen positive rays. G. P. Thomson† considers its usual absence‡ is due to the comparatively small concentration of molecules in most tubes which have been used.

Plate 12
10 hours
Cathode (b)

Plate 10
4 hours
Condensed discharge
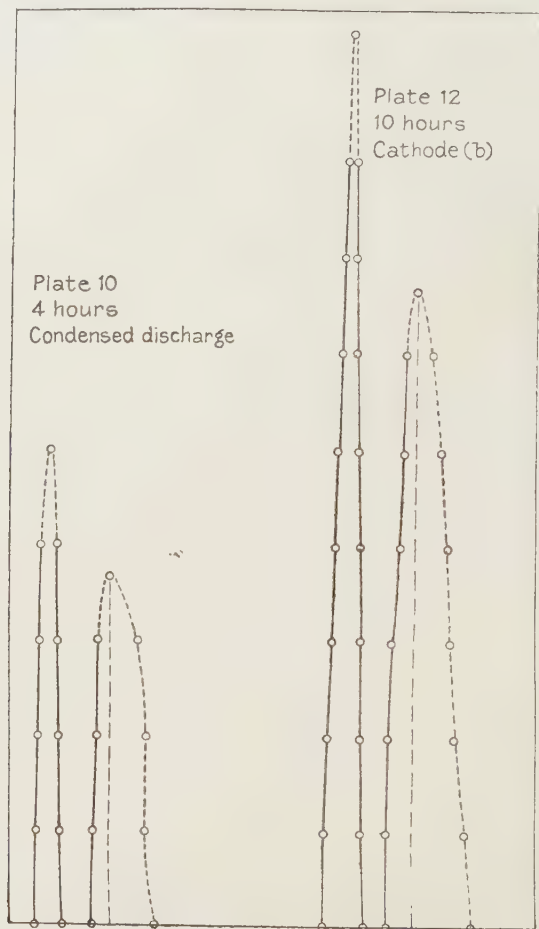
FIG. 3.

In the present experiments the extreme faintness of this spectrum made its examination by the wedge impossible, but measurement of a plain positive-ray spectrogram resulted in the identification of certain lines. In the immediate neighbourhood of H_β the lines found were the ten lines used for calibration in

* Wien : Kanalstrahlen, p. 226 (1923).
† Phil. Mag., 40, 245 (1920).
‡ Vegard : Phil. Mag., 41, 558 (1921).

paragraph 3, with the sole absence of $\lambda 4807{\cdot}33$. Since these were chosen for the calibration because of their intensity in the ordinary discharge tube, their appearance in the positive rays indicates a like intensity distribution under those conditions of excitation.

In addition to these known lines, there is a faint radiation at $\lambda 4853$ showing through the displaced H_β. This is not in Merton's spectrogram and not in the Merton and Barratt list. That it is not a separated intensity component of the moving H_β is shown by its appearance also in comparison spectrograms taken of the same region with an ordinary tube.

A second addition is at $\lambda 4864$, and though not in Merton and Barratt, it is seen in the comparison spectrograms and in Merton's photograph, as well as in the positive rays.

The other possible error in measuring the moving H_β would occur if the sharpness of its edge were increased falsely by a third additional line, which appears near $\lambda 4858$ in the comparison spectograms and in Merton's plate, but not in Merton and Barratt. This, however, is exceedingly faint and far below the intensity of the faintest positive-ray line seen.

None of these 11 lines appear as anything but fine and narrow, as in the comparison spectra : there is no doubt of the absence of Doppler effect in this part of the secondary spectrum even under conditions fulfilling G. P. Thomson's requirement.

The positions of the lines also show that the secondary spectrum cannot contribute to the apparent shape of the moving line H_β.

VI. Comparison with Previous Work.

Several previous investigators have found that the moving line itself in the Balmer series has more than one intensity maximum. Others have found—as in the present experiments—only a single maximum. The appearance of a double maximum has been attributed to the fact that both atoms (H_1) and undissociated molecules (H_2) can be positively charged and accelerated in the positive ray stream. Their velocities will be in the ratio $\sqrt{2}/1$ since the equations governing motion in the dark space are

$$\tfrac{1}{2}m(H_1)v^2 = eV$$
$$\tfrac{1}{2}m(H_2)v^2 = eV$$

The Balmer lines are emitted by the neutral H_1,* but if this atom has until just before emission been undissociated as H_2, the Doppler effect in the line will be that appropriate to the mass of the molecule. A recent research of Blackett and Franck† has made far more plausible the underlying assumption that a hydrogen molecule can be both dissociated and excited to Balmer atomic emission in one simultaneous act.

Unfortunately, the measured ratio of the Doppler displacements at maxima, instead of being equal to $\sqrt{2}$, vary between $1{\cdot}3$ and $2{\cdot}5$. The discrepancies among the results of previous workers in this field make it impossible to ascribe with certainty the maxima in the published curves to H_1 and H_2, and prevent the

---

* Wien : Annalen der Ph., 69, 328 (1922).
† Zeit. f. Ph., 34, 389 (1925).

identification of the hypothetical H_3 of J. J. Thomson[*] with a third maximum seen in some cases.   They also make it necessary to find other criteria to decide whether atomic or molecular carriers are responsible for the results of the present Paper.

Without, therefore, attempting at the beginning to specify H_1 or H_2 as the carriers, comparison with previous work will be made from the ratio of velocity calculated from the Doppler effect to velocity calculated from the potential across the tube.   For the former,

$$v_{\mathrm{D}}=c\frac{d\lambda}{\lambda};$$

for the latter,

$$v_{\mathrm{C}}=\sqrt{\frac{2e}{m}V}.$$

Let v_{D_2} be the velocity at the maximum intensity of the moving line.   Let v_{C_1} be calculated for H_1.

Collecting the measurements of those investigators from whose Papers numerical values can be obtained, we can construct the following table :—

		Paschen.[†]	Wilsar.[‡]	Krefft.[§]	Johnson.
$v_{\mathrm{D}_2}/v_{\mathrm{C}_1}$	Slow max.... ...	0·3 to 0·4	0·2 to 0·4	0·25 to 0·6	0·37 to 0·42
	Intermed. max. ...	...	...	0·4 to 0·6	...
	Fast max.... ...	0·7 to 0·85	...	0·5 to 0·7	...

From this it appears that the single maximum of the moving line in the present experiments agrees with the slower rather than the faster maxima of previous writers.   The identification with slower rather than faster streams is supported by the fact that Krefft finds only the slow stream at the lower voltages, and the faster streams not visible until the voltage is above the highest in the present Paper.

But according to the simple view so far taken to explain these phenomena, namely, that the mass of the singly charged particle is the deciding factor in the speed of the positive ions in the same dark space, the slow stream, with which the ions of the present experiments seem identified, should be that of the greatest mass.   Hence the carriers of the moving spectrum should be hydrogen molecules only dissociated just before atomic emission.

This, however, is disproved by the absence of Doppler effect in the molecular spectrum, which possesses no moving lines.   Further, the fact that three maxima are seen in some curves would, in terms of that explanation, ascribe the slowest maximum, which is very intense, to the rare and unstable H_3 molecule.   A third discrepancy is the fact that Stark and Steubing[‖] find the slower stream increases in intensity relative to the faster stream as voltage is increased.   Krefft finds the

[*] " Positive Rays," p. 202 (1921).
[†] An. der Ph., 23, 247 (1907).
[‡] An. der Ph., 39, 1251 (1912).
[§] An. der Ph., 75, 82 (1924).
[‖] An. der Ph., 28, 974 (1909).

faster maximum increases relative to the slower as voltage is increased. Paschen finds the slower maximum stronger at high voltages.

It becomes necessary, then, to abandon the identification attempted previously, of order of Doppler effect with inverse order of mass, and to seek some other identification of the carriers of the spectrum.

VII. The Carriers of the Spectrum.

Fig. 4 shows the relationship of the velocities measured at different parts of the moving line and the velocities calculated for atomic and molecular hydrogen. The independent variable is conveniently taken as the length of the cathode dark space.

Let v_{D_1} be the smallest and v_{D_3} the greatest velocity in the Doppler effect, and let v_{D_2}, as before, be the velocity at maximum intensity. Let v_{C_2} be calculated for H_2 and v_{C_1}, as before, for H_1.

The graph shows at a glance that while either H_1 or H_2 could give rise to the
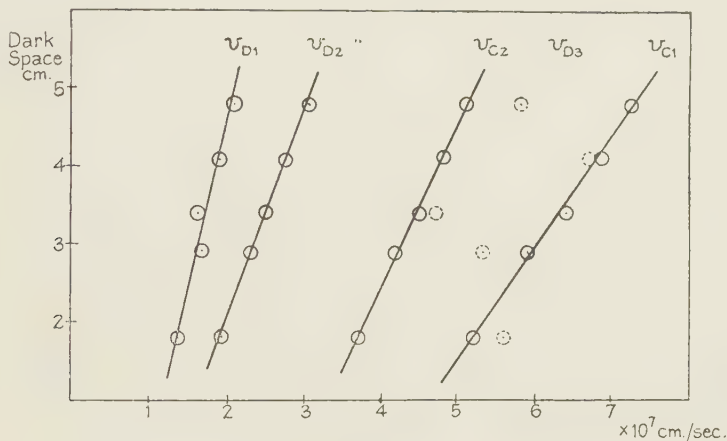
FIG. 4.

Doppler displacement at its maximum intensity or at the smallest separation from the resting line, only H_1 could give rise to the largest displacements. These last, measured on the diffuse edge of the line where the error is greatest, vary so much that the only definite conclusion possible is that they are greater than the calculated value for H_2, which is the highest velocity that could be imparted to a molecule in the tube ; on the other hand, all are smaller than the value for H_1, except one whose excess is well within the limit of error of the measurement at that edge of the line.

Hence, if the spectrograms represent a single stream, the carriers of the Balmer spectrum in the present case cannot have been accelerated as H_2 molecules, as their identification with the slow streams of other investigators would have suggested.

There remains a chance of each spectrogram covering two streams. Paschen's Stream II is diffuse on its violet edge owing to the superposed presence of Stream I at 3,100 volts. But in Paschen's case this asymmetry is transient and only occurs

with the smallest dark space, while here it occurs in all photographs. Hence the present spectrograms cannot be ascribed to a double stream, and must represent the single maximum found by Krefft at these voltages and by Wilsar. The carriers must in that case be atomic.

Once the theory of two streams as atomic and molecular is abandoned, their explanation can be begun on the lines opened by J. J. Thomson,[*] and by Döpel,[†] who investigated electromagnetically the velocity distribution in hydrogen and distinguished two streams, both atomic and isolated from the molecular positive rays. This will not be further discussed here as the present experiments only relate indirectly to multiple streams.

VIII. The Distribution of Velocity.

It is necessary to consider next whether the results obtained can provide any clue as to why the simple order of velocities according to mass of the atomic and possible molecular aggregation does not control completely the Doppler effect.

There are two means of studying the velocities of particles in the positive rays. The Doppler effect shows the velocities of those particles which are emitting light, and the electromagnetic method of J. J. Thomson shows the velocities of the particles which are electrically charged, by analysis of their deflections in magnetic and electric fields.

Now, Retschinsky[‡] has compared the two methods, with respect to the ratios of velocities found thereby to velocities calculated from the fall of potential in the tube. In the parabola measurements he finds velocities which are 15 per cent. lower than the theoretically possible velocities calculated from the dark space. This discrepancy is not as great as those found from the present Doppler velocities at maximum intensity, though it would fit the velocity of Paschen's fastest stream, and would agree with the case of the fastest velocities found in the fainter part of Figs. 2 and 3. Retschinsky and Krefft find no relation between the " beading " of parabolas, i.e., the appearance of several intensity maxima, and the multiple maxima in the Doppler curves of Paschen, Krefft, and Stark.

But a further aspect of the comparison between parabola and Doppler measurements is instructive. The slight asymmetry in the wedge analysis of the latter was shown in Paragraphs 4 and 5 to be unmistakably separable from any contamination by the secondary spectrum : this asymmetry means a preponderance of low-velocity ions in the light emission, since the intensity maximum is near the undisplaced side. Now, hydrogen parabolas can be examined in many examples published by J. J. Thomson and Aston, and most recently in the Paper of Döpel referred to. In the majority of cases there is an asymmetry in the parabola velocity distribution, but in the opposite direction to that in the Doppler effect, i.e., there is a preponderance of the higher velocities, the " head " of the parabola being stronger than the end furthest from the undeflected spot.

J. J. Thomson[§] and Aston[||] explain this asymmetry in the normal parabola

[*] " Positive Rays," p. 85 (1921).
[†] An. der Ph., 76, 1 (1925).
[‡] An. der Ph., 50, 369 (1916).
[§] " Positive Rays," p. 85 (1921).
[||] " Isotopes," p. 29.

distribution by the intense ionisation at the boundary of the dark space furthest from the cathode. A greater proportion of the ions is formed at this boundary than anywhere else in the dark space, and hence there is a concentration of the positive ions about that velocity which is derived from falling through the whole of the cathode fall of potential.

If there were an equal chance of any of these positive ions being neutralised and excited to Balmer emission, the spectroscopic observations should show a similar distribution of intensity—i.e., the moving line should be more sharply bounded and more intense on the violet side. The present experiments show that any asymmetry there is is a sharpness and intensity maximum on the redder side nearest to the undisplaced line.

That this is not due to an individual characteristic of these experiments, appears from its persistence through change of cathode shape, involving change of distribution of the actual positive ion velocity ; especially is this significant in the case of the condensed discharge of Fig. 3. Now the main visible effect of condensing the discharge was to blur the boundary of dark space and negative glow, the former becoming much brighter. This relaxes considerably the condition which J. J. Thomson and Aston laid down for the parabola asymmetry. In spite of this change from the usual distribution of positive ray velocity the opposite asymmetry of the Doppler distribution persists. The conclusion is strengthened that while in the positive ray stream the velocity distribution concentrates a majority round the higher speeds, the greatest number which are neutralised and excited to Balmer emission are concentrated around the lower velocity limit.

We here approach evidently some velocity criterion which decides which of a stream of positive ions can capture an electron.

Rüchardt* has investigated this problem from the point of view of his experiments on Wien's Free Path, the mean distance L_1 traversed by H_1^+ before becoming H_1. He finds L_1 increases with increase of velocity ; this is the physical basis of the distribution we have found in the moving line. Rüchardt states, however, the velocity criterion of neutralisation as follows : The condition for capture of an electron is

$$\tfrac{1}{2}mv^2 \leqslant \frac{e^2}{r},$$

$$r \geqslant r_1,$$

where e and m are charge and mass of electron, v is the relative velocity of ion and electron, and r_1 is the radius of the first Bohr orbit in the hydrogen atom.

This criterion would account for the fact that a Doppler velocity is never more than a certain fraction of the calculated positive ray velocity, but it gives no reason for there not being a sharp violet edge to the moving line in the present experiments. The gradual fading of the violet edge is, however, more definitely accounted for if we adopt as a criterion for capture the law put forward by Milne,† which was suggested by thermodynamics of radiation and fits a large number of astronomical and experi-

---

* Zeit. f. Ph., 15, 164 (1923).
† Phil. Mag., 47, 209 (1924).

mental facts.   According to this law, if P is the probability of an electron being captured when it approaches a positive ion with relative velocity v,

$$P = K_1/v^2,$$

where K_1 is a constant for the atom.

Stated in terms of Wien's Free Path for neutralisation,

$$L_1 = K_2 v^2.$$

IX. The Relative Intensity of Moving and Resting Spectra.

Fig. 5 shows the relation between the greatest intensity of resting and moving lines of H_β.

Vegard* stated the relative intensity of resting lines increased with potential. Dempster† published a series of drawings of intensity curves for H_β, in which the
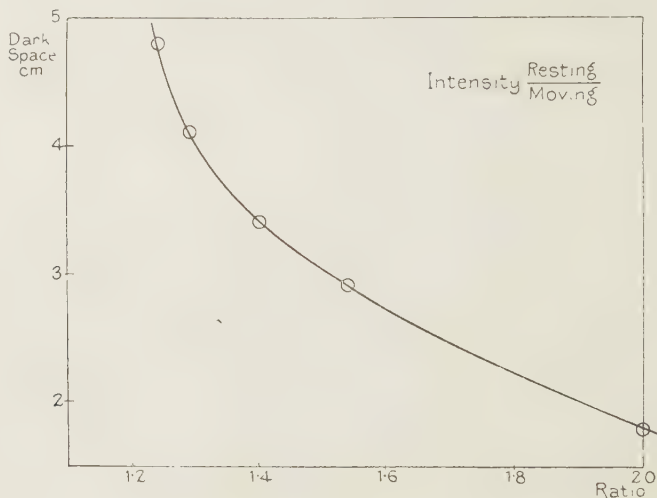
Fig. 5.

ratio of resting to moving intensity increased as the dark space increased.   McPetrie‡ remarks that as the positive ray velocity increases, the moving line intensity diminishes.

These three results are contrary to the phenomenon shown in Fig. 5, where increase of potential increases the moving line intensity towards a limit.

Stark§ found conditions under which increase or decrease of moving intensity are both possible, but he keeps constant quantities which cannot be isolated in the present arrangement.

Vegard, Dempster and McPetrie all worked at higher voltages than those obtained in the experiments from which Fig. 5 is plotted, and so it seems probable that the ratio has a minimum above the highest potential of the present experiments.

* Phil. Mag., 41, 558 (1921) ; An. der Ph., 39, 111 (1912).
† Astroph. J., 57, 193 (1923).
‡ Phil. Mag., 51, 1093 (1926).
§ An. der Ph., 39, 1185 (1912).

and below the lowest of the previous writers. This would be accounted for if two opposing factors underlie this ratio of intensities. In the present state of knowledge the following seems adequate as a hypothesis for both the present and earlier results.

The emission of the moving Balmer line requires the neutralisation of a positively charged atom by capture of an electron. But in the positive ray chamber there is not the free electron concentration there is in the discharge tube, where cathode rays are streaming towards the anode. Wien* and Rüchardt† consider the required electrons are those just previously liberated from stationary atoms or molecules by the impact of ions which immediately capture them.

The emission of the resting line is independent of electron capture, as particles already neutral in the stationary gas can be stimulated to Balmer emission, by inelastic collisions from particles in the positive ray stream, with exchange of less than ionising energy.

If we consider both processes as the result of collision, we are in this case concerned with positive ions as projectiles in place of the electrons of ordinary and thermionic tube spectra ; the energy exchanges required can be classified as follows :

1. For moving line : (a) Ionisation of atom, or (b) ionisation of molecule.
2. For resting line : (a) Excitation of atom, or (b) dissociation of molecule and excitation.

The great strength of the Balmer relative to the many lined spectrum in this type of tube indicates a predominance of the (a) type of process in each case, as in the " red " stage of the ordinary hydrogen tube.

The increase of potential fall in the lengthening dark space of Fig. 5, will correspond to a tendency for 1 (a) to become more common, and a decrease in the ratio of resting intensity over moving intensity will result. A quantitative relation between the two processes, based on the value of the respective critical potentials, cannot be derived, as we are not dealing with a gas in thermodynamic equilibrium.

But if the inverse square law of probability of capture is adopted, the increased number of ionisations by impact will not continue indefinitely to increase the intensity of the moving line. For although more electrons become liberated, the increasing relative velocity of positive ion to electron will decrease the chance of capture by the fast ion, the electrons will tend instead to be captured again by their own or other stationary atoms. At voltages higher than those employed here the ratio of resting to moving intensity will be expected to cease to diminish and begin to rise again, as found by Dempster and others working at very high potentials.

It is a pleasant duty to acknowledge again gratefully the generosity of Prof. S. W. J. Smith, F.R.S., in encouraging and equipping these experiments, and the skill of Mr. G. O. Harrison in instrument construction.

DISCUSSION.

Prof. O. W. RICHARDSON said that, though the interpretation of the author's results might be debatable, there was no doubt as to their importance. The new lines mentioned by the author were in the list published by Tanaka, and there was an additional line within about 1 Å.U. of H_β ; but in view of the author's assurance that the distance between the sharp edge of the moving spectrum and the edge of the resting spectrum, which depended on the voltage employed, was in the neighbourhood of 8 or 10 Å.U., it was clear that this particular line could not be a factor. In fact, he agreed with the author's conclusion that the effects were not vitiated by secondary

---

* Proc. Phys. Soc., 37, 324 (1925).
† Loc. cit.

spectrum lines shining through the moving H_β, all the relevant lines being too weak to affect the observations. He was not convinced that the results afforded very definite support for the law of electron capture suggested by Eddington and Milne. The difficulty he felt was not the diffuse broadening of the line on the side towards the violet, which might occur with many different laws of capture, but the existence on the side towards the red of a sharp limit which did not appear to bear any simple relation to the electric field.

Dr. B. DASANNACHARYA : The pronounced intensity maxima occurring in the displaced line nearer the slower velocities is, I believe, due to the atoms from the dissociation of the accelerated molecules. If, as Mr. Johnson objects and points out, that the maximum velocity which such molecules may attain is lower than the maximum velocity represented in the displaced line, the conclusion is that the atomic stream is to be supposed as existing side by side. The latter is, under the conditions of Mr. Johnson's investigation, weakly represented. Mr. Johnson's second objection to the molecular stream hypothesis is that no Doppler displacement has been observed in the many lined spectrum of hydrogen. Ran actually observed such a displacement in the positive ray behind the cathode by employing a very ingenious method (Wien's " Kanalstrahlen," p. 227). But the effect was very faint, which would justify the assumption that, *behind the cathode,* only a few molecules in the ray are present—in agreement with the results of the electromagnetic analysis—and that the molecules are easily dissociated. In front of the cathode Ran was not able to detect any Doppler displacement of the molecular lines, an interesting fact, from which it has been concluded that the many lined spectrum is due to the neutral molecule, and that in front of the cathode the molecules move as charged particles only, or they must be dissociated.

As regards the double stream theory, Mr. Johnson's objection is that the ratio of the velocities corresponding to the two intensity maximas is not equal to $\sqrt{2}$, but varies between 1·3 to 2·5. The reasons for the variation are the following : The molecules and the atoms in the discharge tube do not behave alike. It is well known that, even in front of the cathode, the canal ray could be seen, which shows that some of the moving atoms of the positive ray, there, are neutral. That the atoms change their state from the charged to the uncharged, and vice versa, is well established. It is obvious, therefore, to expect that the atoms will not get the full acceleration that would correspond to the cathode fall and that the velocity may vary within certain wide limits. The molecules, as I have remarked above, are easily dissociated—the more so the higher the voltage. So it is reasonable to expect the variation of the ratio of the average velocities of the atomic and the molecular streams from the simple value of $\sqrt{2}$.

Secondly, the amount of light given out by an atom in a second is a function of its velocity and the pressure of the gas in the chamber in which the excitation to the emission of light takes place. This is dealt with in a Paper of mine (Ann. d. Phys., 77, 597, 1925), and treated further in a Paper, now in print, in the Journal of Science (Maharajah's College, Vijayanagaram, India). An abstract appears in the reports of the British Association meeting in Southampton in 1925. There is no exact equivalence to be expected between the distribution of the velocity in the Doppler effect and that deduced for the neutral atoms from that for the charged atoms in the electromagnetic analysis. There is also another reason for this difference, because the positive ray traverses a high vacuum in the electromagnetic analysis, whereas for the spectroscopic investigations the pressure is usually of the order of a hundredth of a millimetre of mercury. The curves given in my Paper in Annalen to illustrate these facts are interesting.

AUTHOR'S reply : In reply to Prof. Richardson's question as to why there is a space with no radiation between the resting and moving lines, I believe J. J. Thomson's remark about the minimum energy needed for a positive ray to be effective is the only suggested explanation so far. The rise to maximum on the red side of the moving line appears to represent the same type of probability distribution as the rise on each side of the resting line itself.

In reply to Dr. Dasannacharya, I do not agree that the double maxima have a satisfactory explanation as due to atomic and molecular carriers. The discrepancies between published results for their velocity ratio up to 2·5 and the theoretical 1·4 are what led me to use a new identification method for the carriers. The results in the Paper show that these are all atomic, in spite of agreeing in velocity with the slower stream of the Continental writers, previously regarded as molecular. The mass is not the main controlling factor. In addition to this method for atomic identification, the absence of a molecular stream is shown by the constancy of the smooth intensity curves under all conditions. At one or other of the voltages and pressures used the molecular and atomic maxima would have separated or changed their relative intensity if both were, as Dr. Dasannacharya suggests, present in the single curves.

IV.—A RAPID BOLOMETER MADE BY SPUTTERING ON THIN FILMS.

By H. Dewhurst, *A.R.C.S.*, *D.I.C.*, Imperial College of Science and Technology.

Summary.

Thin Films.—The method of making thin films of collodion by drying weak solutions in ether and alcohol on the surface of clean mercury, and their subsequent removal, is described. Flexible films are also made in the same way, using a modified formula, producing very robust films which withstand great distortion, and will stand being punctured without fracture. Both types can be produced rapidly and cheaply down to a thickness of one wavelength of light.

Sputtering.—Two novel types of sputtering apparatus are described, together with working data. A table is given containing sputtering data for 25 metals, nine of which appear for the first time. Notes relating to the effects of Shape and Age of Kathode, Shape of Anode, Form of Dark-Space and Kathode Temperature appear, together with novel modifications in the design of the Wehnelt break. Approximate temperature coefficients of resistance are assigned to eight new metals and more accurate values to three others, that relating to gold being new. The apparatus used for these determinations is described. Notes and curves on ageing appear regarding six metals and resistances for films of standard size for ten metals. A curve is given throwing, perhaps, some light on the formation of a sputtered film.

Bolometer.—Apparatus is described by which rings are moulded for supporting the thin collodion films and providing a reliable contact for overlying sputtered metallic films. The method of making the bolometers, together with holders of various types, and apparatus for blackening, are detailed. The comparative sensitivity of these new bolometers is discussed, and curves and an empirical formula given from which an estimation of the speed of the instruments can be determined.

The new type is roughly 400 per cent. faster than a representative bolometer of the Lummer and Kurlbaum type. The thickness of the component metal film is estimated.

I. On the Making of Thin Collodion Films.

Object.

FOR the construction of the proposed bolometer it was necessary to devise a method of stretching a very thin film of electrically-insulating material across the aperture of an annular disc. The dimensions of the disc, or ring, were arbitrarily fixed at $1\frac{3}{8}$ in. exterior diameter, with an aperture of $\frac{3}{4}$ in., the thickness of the annulus being $\frac{1}{8}$ in.

Question of Suitable Material.

The most promising material of which the thin film could be made appeared to be one of the following : Mica, glass, celluloid, gelatine or collodion. No Papers dealing with the production of very thin films in a permanent form seemed to have been published, with the exception of one dealing with films of gelatine and soap,* which would be much too thick for the purpose in view.

It may be interesting to describe very briefly how thin films of mica and glass were obtained ; which, although thin enough to show interference colours, were otherwise unsuitable. The method adopted in the case of mica was the successive

---

* "Durable Films," R. Malagoli, N. Cimento, 11, pp. 351-53.

splitting of a thin sheet. The mica was "sandwiched" between two plane brass plates, with a film of adhesive between each plate and the mica face adjacent to it. When the adhesive had set sufficiently the plates were pulled apart ; the process to be repeated as often as necessary with the successively thinner sheets of mica.

It is clear that the adhesive used must effect a greater cohesion between metal and mica than that one can imagine to exist between adjacent mica laminæ. Of the adhesives tried—shellac, shellac and beeswax, "Chatterton's compound" and sealing wax—only the latter was successful. Contrary to expectations, the mica usually split the first time, leaving a film on one metal plate sufficiently thin to show interference colours. Unfortunately, the film thus obtained was not of uniform thickness. The whole area was split up into small patches, each of uniform colour, bearing a resemblance to an aerial photograph of country divided up into a number of fields. The average thickness of the mica, however, was of the required order ; but on attaching the annular ring and dissolving ring and film away from the metal plate in alcohol, the various small areas of uniform thickness broke away from their neighbours, the whole film thus disintegrating. Mica, therefore, was unsuitable for the purpose in view, unless specimens could be obtained containing fairly large areas of uniform thickness in some particular well-defined lamina. As, however, such laminæ would be distributed in depth in the thickness of the mica, the chances of finding one in the right location for splitting were very remote.

In the case of glass the ordinary method of blowing a sphere would be inadmissible, as it would be necessary at a later stage to attach flat electrical contacts to the finished film, the curvature of the glass making this impossible. The method tried, therefore, was that of blowing two bubbles at the same time, both pieces of the molten glass used for blowing being connected to the mouth through rubber tubes of the same diameter by means of a Y-piece. If the expanding spheres of glass touch each other when of the same size, thickness and temperature one would expect a plane film of double thickness to result. It is, however, practically impossible to get all the conditions for success fulfilled at one and the same time. In the one case in which a reasonably flat film was obtained it was found that the glass was corrugated in circular waves, these being due to the imprisonment of air between the two component glass films.

There remained celluloid and similar substances which could be dissolved in some solvent, the solution spread over a plane area, leaving a thin film on evaporation of the solvent. It was known that thin celluloid films were being made* by a process, no details of which appear to have been published, using rock-salt. A solution of celluloid is poured on to an optically flat face of a rock-salt disc, allowed to dry, the rock-salt being finally dissolved away in water, leaving the film attached to (say) a ring, which had previously been stuck on the film-covered face of the rock-salt. This process, whilst not giving very uniform films, is a lengthy and very costly one ; both factors rendering it prohibitive in the present case, where a large number of films would be required for tests to destruction.

A modification was therefore tried in which the celluloid or collodion solutions were poured on to the surface of water and allowed to dry. In both cases the solvents used were soluble to a greater or less extent in the water itself, thus tending to lack of uniformity in the films produced.

* Adam Hilger, Ltd.

Outline of Method Adopted.

At this stage mercury was substituted for water, this proving to be the basis of the successful process to be described. Collodion was finally adopted in preference to celluloid, owing to the greater standard purity in which it could be obtained. Gelatine was ruled out, owing to the time required for water solutions to dry. Briefly, then, the method finally used was the pouring of a few drops of a weak collodion solution in ether and alcohol on to a clean surface of mercury. The solution spreads, forming a disc which dries very rapidly, usually from the periphery to the centre. Just before the film is quite dry the annular ring which is to hold the film is placed on top of the film-covered mercury, the surplus film outside the ring removed, and finally the ring and film taken off the mercury as described later.

Factors Affecting the Final Product.

The collodion used was that known commercially as " Mawson's." This is a somewhat viscous solution, and requires considerable dilution before use. Dilution by ether alone, after a certain point, gives an imperfect solution, and consequent cloudiness. The addition of a small quantity of alcohol, however, effects a perfect solution. The amount of alcohol permissible is rather critical. Too high a proportion of alcohol gives films which contract and corrugate on drying ; too high a proportion of ether, on the other hand, giving whitish films instead of the usual clear product. A solution sufficiently dilute to give a film showing interference colours on drying was found by rough trial. Such a solution, however, will only give consistent results provided the mercury surface is absolutely clean and the collodion solution reasonably pure. The slightest trace of contamination on the mercury surface, whether due to grease, moisture or amalgams, is fatal. Contamination prevents the solution " wetting " the mercury surface. Unless the solution wets the mercury properly, gravitational action will be insufficient to spread the solution ; one being left with a small, oily, distorted result bunched together by its surface-tension, whose drying will be slow and restricted, with consequent variation of the mutual proportion of the two solvents. It is not surprising that under these circumstances a sticky white film will result, and of a thickness greater than that normally obtained.

The following proportion of the constituents was found to give good results :

Mawson's Collodion	...	...	...	...	1·0 ccs.
Ether (anæsthetic)	...	...	...	...	9·5 ccs.
Alcohol (absolute)...	...	...	...	...	0·5 ccs.

the two solvents being first mixed together and the collodion then added. Standardising the solvent proportions, a decrease in the collodion content tends to make messy and fragile films.

The rate at which the solution is allowed to dry is very important. Rapid drying gives clear films of uniform colour, whereas slow drying produces oily, contracted and unevenly coloured results.

As contamination of the mercury used has such a deleterious effect on the final product, the mercury has to undergo several cleaning processes before it is suitable for film making. It is twice passed, in a finely divided condition, through dilute nitric acid, and twice in a similar manner through distilled water ; being

finally distilled in a partial vacuum whilst a slow current of air passes through the boiling liquid to oxidise base metals.*

Solid contamination is removed by " filtration " through a small hole in the apex of a folded filter-paper in the usual manner. This gives better results than squeezing through chamois leather. The presence of grains of dust, fibre, etc., on the mercury, however, is by no means so serious as other types of contamination, and, even if present, can always be removed by forming a film over the foreign matter and stripping both from the surface. In fact, this method would appear, from the experience gained, to be the most certain method of obtaining a perfectly clean surface. It should be noticed that filtration must always immediately precede film making, whereas the washing and distillation as described need only be carried out once for any given batch of mercury.

Detailed Method of Film Production.

The mercury is contained in a glass funnel sealed at the apex of the cone (Fig. 1). A containing vessel of this shape gives sufficient depth for the operation of removal to be described, whilst at the same time necessitating the use of considerably less
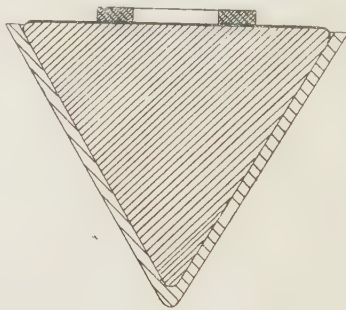
Fig. 1.—Simple Apparatus for making Thin Collodion Films.

mercury than would be required to fill a cylindrical vessel to the same depth. More important still, the funnel shape decreases very considerably the liability to circular waves being set up on the surface, due to adventitious shaking ; such waves tending to puncture the film in the centre.

The collodion solution is poured on to the mercury by means of a 1 cc. pipette. Roughly, $\frac{1}{3}$ cc. is allowed to fall in a continuous stream. The solution first spreads rapidly, and afterwards more slowly, until the increase in size is held up by drying or the walls of the funnel. Drying proceeds in waves, beginning at the periphery and ending at the centre, and becomes visible owing to the change in tone. The last wave leaves a clear iridescent film quite distinct from the dull appearance of an imperfectly dried film. It is just before the final disappearance of this dullness at the centre that the ring should be placed on the film. Too long a time elapsing between the drying of the film and the placing of the ring will involve a lack of adhesion between the two, rendering it impossible to remove the film from the mercury surface. The superfluous film round the outside of the film can now be removed by means of a needle. The process by which the ring and the film are

* " Practical Physics," W. Watson, pp. 487-9 (1917).

removed from the surface is illustrated in Fig. 2. A fairly large globule of mercury is poured gently into the aperture of the ring, so that the film at the bottom is sand-wiched between mercury (Fig. 2A). The ring is now pushed down at one side below the surface until the mercury above and below the film has joined together (Fig. 2B). The ring is tilted further, whilst keeping the film whol'y below the surface, until the ring is vertical, when it can be lifted straight up out of the mercury, with the film stretched across it (Fig. 2c). By this means the pressures and surface-tensions on both sides of the film are maintained practically the same throughout. Collodion films are so tightly stretched when dry, and are so slightly extensible, that a very small distortion is sufficient to break them. Occasionally one can mani-pulate them with sufficient skill to slide them horizontally off the convex boundary of the mercury surface. The method is a very uncertain one, however.

It will be found that in many cases tiny pellets of mercury are left adhering to the ring, and in some cases (when the mercury is insufficiently clean, or the film not properly dry before removal) to the actual film itself. In both cases they can be removed by wiping carefully with a small pledget of very wet filter paper.

Once all the necessary conditions for success, as outlined, have been obtained, the process is a quick one, the time necessary to produce a film being only two or three minutes. It will often be found, however, that, although all the precautions
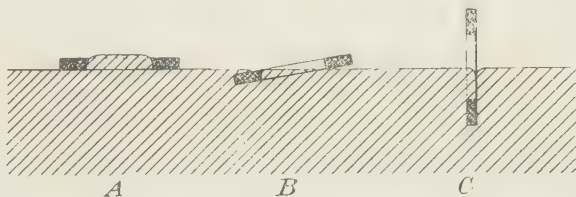
FIG. 2.—METHOD OF REMOVING THIN FILM FROM MERCURY SURFACE.

have been taken to ensure clean mercury and a properly working solution, several films will prove unsuccessful, and must be removed one after the other until the surface has become sufficiently clean in the process. In all cases the first film is abortive, thus lending additional weight to the assertion that the removal of a film from the surface leaves it in a much more perfect state of cleanliness than is obtained by the more usual methods. It is important to notice, also, that succeeding films, to be successful, must be made more or less immediately.

Flexible Thin Films.

It has been mentioned that films made by the above process were tightly stretched and inextensible. Owing to this reason they were found quite unsuitable as a base upon which a thin metallic film could be formed by the process of "sput-tering." A large number of films were tried under sputtering varied in every way possible, but in all cases the films were shattered by the particles hurled from the kathode. It was necessary, therefore, to devise some modification of the film formula, or make use of some new material, which would result in films that were flexible and which would not shatter when punctured. The solution of such a problem would lie, in the first place, in the trial of various promising substances which, when added to the collodion, would confer the property of flexibility.

Success was attained with the addition of critical proportions of Canada balsam

and castor oil. Neither of these alone will confer the requisite property of flexibility, for, as will be seen immediately, the addition of the balsam results in white brittle films, whereas the oil gives oily and sticky products. In retrospect, it is rather remarkable that a formula should exist at all which will give films sufficiently tough to withstand the kathodic bombardment of sputtering, but yet, at the same time, prove amenable to the very delicate process of thin film making. The data will now be quoted relating to the effect of variation of the constituents from considerations of which the final formula was eliminated.

For convenience, arbitrary standard solutions of the constituents were made up, these being given short pseudonyms to obviate unnecessary repetitions. It will be convenient to retain these names for the purpose of this Paper. The solutions were :—

      40 per cent. solution of Mawson's Collodion in ether.   " Collol."
       2   ,,   ,,   Canada balsam   ...   ...   " Balsol."
       1   ,,   ,,   castor oil   ...   ...   " Castol."
       5   ,,   ,,   ethyl alcohol   ...   ...   " Ethol."

Although, of course, a large number of experiments were carried out to obtain the best proportions, only a few of the more conclusive ones will be outlined here.

Preliminary trials had shown that the probable composition would lie between the values :—

Collol.	*Balsol.*	*Castol.*	*Ethol.*
0·5 to 2.	0 to 2.	0 to 2.	2·5 ccs.

Experiments were therefore made using 0·8 to 1·0 ccs. of collol. Additional alcohol was found necessary to the extent of about 0·3 ccs. in order, possibly, to allow for the complete solution of the additional balsam and oil. Tabulated results follow of a series of films in which the proportions of the balsam and oil to each other were varied, whilst other factors were kept constant.

TABLE I

Solution.	Collol.	Balsol.	Castol.	Ethol.	Alcohol.	Spread.	Drying.	Removal. Condition.	Removal. Flexibility.	Film Char. Colour.	Film Char. Clarity.
1	0·8	0	0	2·5	0·3	Normal	V. good & fast	V. clean corrugated	Tears easily	V. bright	V. good
2	...	0	2	...	...	...	V. uneven & spotty	V. oily ...	Sticky ...	...	Poor
3	...	2	0	...	...	...	Con-tracts	V. white	V. brittle	None ...	Bad
4	...	2	2	...	...	...	Fair ...				
5	1·0	2	2	...	...	...	Good ...	V. oily ...	Sticky ...	Poor ...	Poor
6	...	1	2	...	...	...	...	Clean ...	Tough ... Tears easily	Fair ...	Good ...
7	...	2	1	...	...	...	...	V. white	V. brittle	None ...	Bad
8	...	1	1	...	...	...	...	White ...	...	Poor ...	Poor

In the first four, 0·8 ccs. of collol were used, whilst in the last four this was increased to 1·0 in order to reduce the proportion of the balsam and oil combined to that of the collodion. It will be noticed that while none of the films 1 to 4 is at all satisfactory, 2 indicates that an excessive quantity of castor oil makes the resultant film oily and sticky, while excess of balsam confers a white brittleness quite fatal to flexibility. Film 5, owing to the increase of the collodion to balsam-and-oil ratio, is very nearly up to requirements, the lack of brilliance in the interference colours indicating the possibility of too heavy a proportion of balsam and oil combined to the remaining constituents. Films 6 and 7 merely tend to confirm the conclusions arrived at from 2 and 3.

Using film 5 as a basis, experiments were made varying the proportion of ethol by 50 per cent. each way, retaining the 1 cc. collol, 2 ccs. balsol and 2 ccs. castol ratio. The results were somewhat inconclusive, and point to the proportion of ethol not being a critical one. Retaining, therefore, the proportion of ethol at 2·5 ccs., the ratio of balsam and oil were varied within a narrower range. In the first series, retaining the balsol at 2 ccs. throughout, the castol was tried between 1·6 and 2·4 ccs., by steps of 0·2 ccs. at a time. Secondly, keeping the castol at 2 ccs., similar variations in the balsol were experimented with. In both cases the best result was obtained when there was 0·2 ccs. less balsol than castol. Thus the best films in each series were obtained from :—

	Collol.	Balsol.	Castol.	Ethol.	Alcohol.
(1)	1·0	2·0	2·2	2·5	0·3 ccs.
(2)	1·0	1·8	2·0	2·5	0·3 ccs.

As a last preliminary, the amount of collol was varied, retaining the other proportions according to either of the above, between the limits 0·6 and 1·4 ccs. From the results it appeared that 1·2 ccs. met the case to a better extent than the others.

Having by a method of successive approximations arrived at a formula presumably approaching the best possible, a final trial, tabulated below, was undertaken to obtain the best mutual proportion of the balsam to oil—the most critical factor.

TABLE II.

Solution.	Collol.	Balsol.	Castol.	Ethol.	Alcohol.	Spread.	Drying.	Removal. Condition.	Flexibility.	Colour.	Clarity.
1	1·2	1·8	2·0	2·5	0·3	Normal	Uneven, slow	Clean ...	Tough ...	Good ...	Good
2	...	1·6	2·0	...	...	...	Fair ...	...	...	...	...
3	...	1·4	2·0	...	...	...	Good ...	Inclined oily	...	...	...
4	...	1·4	1·8	...	...	...	...	Clean ...	...	...	...
5	...	1·4	1·6	...	...	...	...	Inclined oily	...	...	...
6	...	1·2	1·8	...	...	...	Fair ...	Clean ...	Inclined brittle	Fair ...	...
7	...	1·2	1·6	...	...	...	...	...	Inclined to tear	...	...

Of the seven films above it will be seen that only one gives a really satisfactory film all round, whereas all the others have some factor or factors precluding their use. Reducing the values in film 4 to terms involving only the original constituents, the composition of the solution giving satisfactory flexible films will be :—

Collodion	...	...	...	...	...	...	0·48 ccs.
Canada balsam ...	...	...	...	...	...	0·028 ,,
Castor oil	...	...	...	...	...	...	0·018 ,,
Ether	...	...	...	...	...	...	6·25 ,,
Alcohol ...	...	...	...	...	...	...	0·43 ,,

It is not asserted that other combinations are not so good, nor even better, perhaps, for the purpose required ; but the above formula appears to work well under most conditions (all the usual precautions being observed), whereas other solutions, which on occasion give equally good results, may be found useless, as, for example, in a humid atmosphere.

Later experiments were performed using 10 per cent. ethol, thus obviating the addition of 0·3 ccs. of alcohol on each occasion.

It is to be noticed that in the case of these flexible films removal can be effected in all cases by sliding horizontally off the mercury surface. They are, in fact, so extensible that they may be distorted into hemispheres by blowing without fracture ; in addition, they may be punctured by needles, for example, and prove self-sealing (in the case of small holes).

Thickness of Collodion Thin Films.

Interferometer tests have shown that the collodion films made as above are roughly two wavelengths of sodium light in thickness—i.e., approximately 0·00011 to 0·00012 cm.

A later type of film was made of roughly one-half the above thickness, a modification of the film-formula being the addition of 7 ccs. of 10 per cent. ethol, instead of the previous 2·5 ccs. in the standard case. It was clear that the " black film " stage was very near, as the films were a deep yellow by reflected light, and in one or two cases actual blackness was attained. Interferometer tests confirmed this, the thickness being of the order of one wavelength only, although any accurate measurement for displacements of only one wavelength are, of course, precluded. The thickness of the later type of film was therefore half the previous value, or roughly 0·00005 cm. It was noticed in the case of the black films that they were extremely brittle and had very little cohesion. It therefore seems probable that the limit has been reached in the thinness of films made by the method outlined. The standard thickness type of film and the latter half-thickness type were both used in making of bolometers.

<div style="text-align:center">II. On Sputtering.</div>

Outline.

The thin collodion films obtained by the process already dealt with, and mounted on an electrically non-conducting flat annulus containing two metal inlaid contacts, had now to undergo the process of " sputtering," or kathodic deposition, in order to lay a very thin strip of metal from contact to contact across the collodion film. The changes of resistance of this metal strip or film, resultant upon changes of temperature due to the absorption of radiant heat, constitute the principle of the bolometer.

Sputtering, as a method of depositing metals in mirror-like films, has been known for about fifty years, although, even now, we are not too well acquainted with the laws governing the process. A comprehensive treatment of the subject, together with an exhaustive bibliography up to 1912, is contained in a Paper by Kohlschutter.* A general summary, including the above, appears in an article by Kaye,† which forms a useful basis of information for work on this subject.‡

The present Paper does not treat of sputtering, or any of its phases, in particular ; but merely records observations made whilst using the process as a means to an end—viz., the production of a new-type bolometer. Consequently, observa-
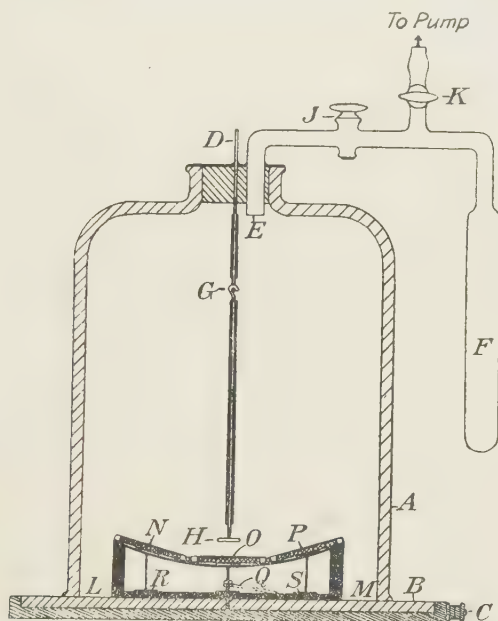
FIG. 3.—APPARATUS USED FOR SPUTTERING ON THE THIN FILMS.

tions relative to sputtering alone will be mentioned only when they supplement, confirm or refute earlier work.

Apparatus and Process Adopted.

The apparatus used in the first instance is represented in section (Fig. 3 §). This consists of a bell-jar (*A*) resting upon a plane ground glass (*B*), the latter provided with a metal base and terminal (*C*). The aperture of the bell-jar is closed with a rubber cork, whose top is covered with a smooth layer of sealing-wax, forming an airtight joint. Through the cork pass an aluminium kathode (*D*) and a glass tube (*E*), leading through glass taps to the pump and charcoal-tube (*F*). Inside

* Jahrbuch d. Radioact, 9, pp. 355-418 (1912).
† Chemical World, 11, pp. 149-52, 183-5, 211-4 (1913).
‡ *See* also F. Simeon, Phys. Soc. and Opt. Soc. joint discussion, p. 26 (Nov., 1920).
§ All the diagrams of apparatus in this Paper are to scale, and therefore actual dimensions of components can be ascertained from the drawings if it be remembered that the diameter of the sealing-wax rings, which occur explicitly or implicitly in each, is $1\frac{3}{8}$ in.

the bell-jar the kathode is broken at the swivel-joint (*G*), the lower part consisting of an aluminium rod attached at the end to a rectangular slab (*H*) of the metal to be sputtered. The aluminium wire, except at the swivel, is clothed with glass tubing to heighten the kathode-fall of potential at the end of the electrode. Underneath the kathode is the "sputtering-table," the top of which is a rectangular strip of mica, whose length is bent into the arc of a circle, centre *G*, and is supported at each end by upright pieces of ebonite fixed to an ebonite base-plate. Along the top of the mica are three strips of aluminium foil, about $\frac{1}{2}$ in. wide, running parallel to each other across the width of the mica. Similar aluminium strips are fixed to the ebonite base-plate, vertically below those on the mica, each pair being connected by a vertical aluminium wire at one edge of the table. Fixed to the ground-glass base, and connected electrically to the metal base-plate, is a selector contact (*Q*), which swings about a vertical axis, and can be brought to rest by tilting the apparatus upon any one of the three strips on the ebonite base-plate. The metal base-plate being the anode, it is clear that any of the three strips on the mica table-top can be connected to the anode, to the exclusion of the other two. Resting upon each strip of the table-top is an aluminium mask (*N, O, P*), sketched in Fig. 4 (shown upside down),
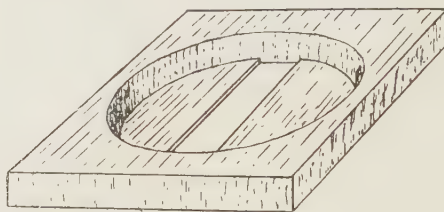
FIG. 4.—SPUTTERING MASK.

covering the rings and films to be sputtered, the aperture of each mask being in the shape of a long slit ($\frac{1}{4}$ in. wide), overlapping at each end the two contacts inlaid in the ring below.

Briefly the process of sputtering is as follows : The primary of an induction coil (4 in. spark) is connected in series with a Wehnelt interrupter to a lighting circuit (110-220 volts), the secondary being connected, through a thermionic rectifier,* to the electrodes of the sputtering apparatus. The vacuum pump (Gaede oil) is put in connection with the charcoal tube by closing tap *J* (Fig. 3) and opening tap *K*, the charcoal being raised to a dull red heat by means of an electric heater. The latter is now removed, and, the charcoal being cool again, tap *J* is opened and the bell-jar pumped out. Liquid air is applied to the charcoal tube until the dark space round the kathode has a radius of between 1 and 2 cms. In general, under these conditions, sputtering takes place and a metallic film of the same shape as the mask aperture will be deposited on the collodion film.

Follow the experimental data which governed the design of the apparatus used and the process adopted, where such are of interest or show novelty.

It will facilitate matters if one divides into five arbitrary groups the factors affecting the process of sputtering. These factors are : Nature of kathode, kathode fall of potential and gas pressure, current density, nature of the gas and temperature of the kathode.

* Mullard, " U.30."

Nature of Kathode.

Due to the fact that most metals appear to have a very much smaller temperature-coefficient of resistance in the sputtered condition than that which they have normally, a large number were tried to find one with a coefficient sufficiently large for the purpose in view. No quantitative results* of any great practical value have appeared relating to the amount of any particular metal that will be sputtered under given conditions, owing, doubtless, to a very real difficulty in specifying the conditions. Qualitative lists have, however, been quoted by several writers, giving the order of facility in which sputtering takes place. The first is that given by Wright[†] in 1877, he apparently being the first to investigate the subject. His list in order of facility of sputtering is :—

(1) Bi, Au, Ag ... ... (readily)
(2) Pt, Pd, Pb, Sn, Zn, Cd ... ... (less readily)
(3) Cu, Fe, Ni, Co ... ... (with difficulty)
(4) Al, Mg ... ... (very difficult)

From this table he draws the conclusion that the heavy metals are more readily sputtered, whilst fusibility, tenacity and electrical conductivity all appear to exert some influence. Crookes,[‡] in 1891, gives his list :—

Pd, Au, Ag, Pb, Sn, Pt, Cu, Cd, Ni, Ir, Fe, Al, Mg,

which differs somewhat from that of Wright, and which he notes as being roughly in order of the voltaic series. Holborn and Austin,[§] and also Kohlschutter,[‖] state that, other things being equal, the amount of sputtering is roughly proportional to the chemical equivalent. These divergent opinions are not, of course, intended to be taken too seriously ; and one would say that the actual physical phenomena involved in sputtering are, as yet, little understood.

Comparative results of a large number of the present experiments, conducted under fairly constant conditions, are tabulated below :—

TABLE A.

Vapour-izes.	Melts.	Thick deposits possible.		Thin deposits.	Very faint deposits only.	No appreciable deposits.
		Readily.	Not so readily.			
Hg*	Wood's* metal	Bi	Cd	Ir	Mn*	W
		Bi*(alloys)	Ni	Sn	Cr*	Al
		Au	Tl*	Pd	Zn	Se*
		Pt	Te*		Fe	
		Ag	Co		As*	
		Pb				
		Cu				

The metals marked with an asterisk (*) have not, apparently, been previously investigated.*

* Since writing this Paper some valuable quantitative results for 25 metals have appeared, together with a very possible law relating these. *See* A. Güntherschulze, Zeit. f. Physik. 36, p. 563, Nov. 8, and 38, p. 575, Nov. 8 (1926).
† Am. Jour. Sci. and Arts, 13, pp. 49-55 (1877).
‡ Proc. Roy. Soc., 50, 88 (1891).
§ Wissensch. Abhandl. d. Phys. Techn. Reichsanstalt., Bd. 4, p. 101 (1904).
‖ Loc. cit.

Apart from mercury and "Wood's metal," which will be dealt with later, it will be seen that bismuth heads a list of seven metals, all of which sputter readily to give thick, opaque films, if and when required. (The bismuth alloys were with tin and silver.) Five others follow which will give similar films, but require a longer "exposure" in which to do so. The first group require a period ranging roughly from ten minutes to half-an-hour, under the conditions to be specified later, whereas the second require from one-half to three hours. Up to a period of three hours the . remaining metals give the results indicated. A few peculiarities should be noted. Tellurium deposits in a widespread manner, covering the whole of the bell-jar interior, whereas the deposition of other metals is more or less confined to the nearest object whose surface is normal to the direction of sputtering. Zinc and arsenic both scintillate vigorously, the former, however, only during the first few minutes. Selenium dilates, as if on the point of melting.

In the case of mercury the electrodes were reversed, the liquid being contained in a watch-glass supported on the mica table-top (kathode), with the collodion film (anode) suspended above it. Under the action of the discharge, the mercury was apparently in a state of ebullition, volatilization being widespread over the bell-jar. Something of the order of grams of mercury was sputtered in a few minutes ; in all cases the greyish deposit coagulating into beads of all sizes. This experiment, which does not appear to have been carried out previously, offers, it is thought, striking confirmation of the theory that sputtering is a form of volatilization.*

Eliminating the metals not common to all, the table just quoted agrees with that of Wright in placing bismuth at the head of the list and palladium lower down, whereas agreement is closer with that of Crookes in placing copper and nickel higher. In the case of tin a lower value than in either of the others is assigned. Even if one constructs a table embodying the mean results of the three lists, it is difficult to find confirmation for any of the suggestions advanced as to the order being roughly that of the voltaic series or proportional to the chemical equivalents.

From considerations of the present experiments, it would appear that metals in Groups I, II and VIII of the Periodic System, together with the metals of high atomic number—Hg, Tl, Pb, Bi (11th row)—sputter with greater freedom than the majority.

Nature of Kathode : Minor Factors.

There are other factors of experimental importance which effect the deposition of metals. These are age of kathode, shape of kathode, shape of anode and form of the dark space.

It has been stated that the previous history of the kathode is of no importance ;† in other words, that old and new kathodes would sputter to the same extent under otherwise similar conditions. The present experiments do not tend to confirm this, for it is found in the majority of cases that the deposit obtained from a second sputtering immediately following a previous one is superior in quality and obtained with greater freedom. One may instance the case of bismuth. An electrode of this metal, unused for a few weeks, gave with difficulty a black film, whereas an immediate repetition yielded the usual mirror-like deposit characteristic of sputtered metals. One can only credit the phenomena to the formation of a film of oxidation, to the adsorption or condensation of gases, or to all of these.

* A. C. Longden, Phys. Rev., 11, p. 40 (1900).
† A. M. Tyndall and H. G. Hughes, Phil. Mag., 27, pp. 415-27 (1914).

The shape of the kathode is of importance, especially as regards the uniformity of the deposit obtained. That this is so follows from the conception, usually adopted, of sputtered particles leaving the kathode surface normally and travelling in straight lines. One expects, therefore, the shape of the sputtered film to be similar to that of the kathode. A rectangular electrode will, in general, give a rectangular image (somewhat blurred), and so on. Since, however, the sputtered particles are negatively charged, they will only deposit freely on surfaces which are positive to the kathode. The shape of the anode is therefore a factor in the modification of the shape of the resultant sputtered film. Again, the shape of both electrodes will affect the kathode-fall of potential, which is a vital factor in the rate of sputtering obtained. As an example, in these experiments all kathodes were rectangular plates (with a few exceptions), of dimensions slightly greater than those of the mask through which sputtering was to take place. In most cases uniformity of deposit was thus obtained. In one or two instances, however, where the anode distribution of potential had been modified by some means or other, it was found that greater uniformity was attained with the length of the kathode at right angles to the length of the mask.

The shape of the dark space is dependent, of course, on that of the electrodes and on the kathode fall of potential. It has been stated that no deposition will occur inside the dark space.* This statement would appear ambiguous, for the dark space will always be delimited in the proximity of the anode. For unrestrained deposition a surface positive to the kathode is required. A kathode then, although surrounded normally by a dark space of an inch, say, will yet deposit on an anodic surface at a distance of less than an inch.

It is important to notice, however, that in the present case, where sputtering is to take place on non-conducting collodion films, it is always advisable to use a kathode distance in excess of the dark-space depth, as it will be very difficult to maintain the film within the dark space sufficiently anodic to the kathode. In such a case it is only too true that sputtering will not occur within the dark space, although matters are changed once a preliminary thin deposit of metal, connected to the anode, has been sputtered on the collodion film.

Other Factors Affecting Deposition.

In the case of kathode fall of potential and gas pressure,†‡§ no quantitative experiments were made, although qualitative remarks concerning them will appear later on. The relation between current density† and the rate of sputtering was not determined ; whilst all the present data were obtained from metals deposited in air (nature of the gas).†‡§

Kathode Temperature.

Recent work has shown that, in the case of tungsten, the temperature of the kathode has no effect on the rate of disintegration.‡

On the other hand, Crookes found that, in the region of the melting point, the rate of sputtering is markedly increased in the case of the less refractory metals — tin, cadmium and lead. In the present experiments the effect of the discharge on Wood's metal is striking. This alloy is rapidly melted within a minute or so of the

* Kaye, loc. cit.
† Tyndall and Hughes, loc. cit.
‡ Research Staff, G.E.C., Phil. Mag., 45, pp. 98-112 (1923).
§ Kingdon and Langmuir, Phys. Rev., 20, p. 107 (1922).

discharge being started. It is very doubtful whether the temperature of the metal is actually raised to the melting point, especially when one remembers the case of mercury, already quoted, in which the liquid was apparently in a state of ebullition, although the temperature could not conceivably be in the region of the boiling point. One can only conclude that sputtering is a form of electrical evaporation without considerable rise in temperature ; the temperature of the kathode being of little importance, except where it approaches that of the boiling or melting points of the metal concerned, in which case the amount of sputtering is increased out of all proportion.

Apparatus Detail.

Referring back to Fig. 3, the apparatus and method adopted can be examined in greater detail in the light of data obtained. Here, as in other later instruments, temporary vacuum-tight joints were made by using soft red wax. The wax is prepared for use by being squeezed through a small circular aperture into the form of a long thread. A piece of this thread would be attached all round the ground glass opening of the bell-jar (L, M), the latter being then placed on the ground-glass plate B. On applying the pump, the thread is squeezed into a wax tape, which effectively seals the apparatus. The function of the swivel joint at G is two-fold. By tilting the whole instrument one is enabled to present the kathode H opposite any of the three masks (N, O, P) containing films to be sputtered. Usually the centre mask is left vacant, so that a preliminary sputter, in the position shown, will ensure the kathode being rendered clean enough to give a normal deposit with discharges immediately following. By tilting the instrument the kathode will swing into position opposite to either N or P, thus enabling one to sputter two films in turn with only one evacuation of the jar. As it is found that sputtering deposits most freely on surfaces positive to the kathode, it is expedient to make the film to be coated as positive as possible, and to reduce otherwise the area of anode surfaces within the jar. This is achieved by the selector attachment previously described. When the jar is tilted to the right, the moving selector-contact Q will rotate on to the aluminium strip S, which is connected by a wire to the aluminium strip P, immediately under the film to be sputtered. At the same time the other four aluminium strips on the sputtering table are disconnected from the anode. (Adjacent masks are insulated from each other by wax threads.) This device tends to more rapid deposition than when no precautions are taken to reduce useless anode area ; and considerably more than when no steps are taken to make the film positive.

In general, the conditions under which sputtering was conducted were as follows : Discharge current, 7 millamperes ; dark space, 1 to 2 cms. ; kathode distance, 2 to 3 cms.

It is found that currents in excess of 10 milliamperes, or gas pressures of less than that associated with 2 cms. dark space, appear to give black non-conducting deposits.

Wehnelt Interrupter.

A modified form of this break was designed for use with the sputtering apparatus. With the usual type, trouble is experienced in burning out the platinum anode. In addition, variations in the current strength are not permissible to any extent ; the sulphuric acid electrolyte becomes vitiated after a time, making long runs of an hour or more impossible ; and the temperature of the electrolyte rapidly

increases. The design finally evolved, shown in Fig. 5, consists of a glass jar (*H*) containing an electrolyte (*A*) composed of a solution of one part phosphoric acid in seven parts of water. This constitution remains unchanged, excepting the evaporation of water, there apparently being no chemical changes taking place in this instance. More important still, the break works indefinitely.

The electrolyte is cooled by the lead helical piping (*B*), through which flows cold water, the piping also acting as the kathode. A novel feature is the form of anode. Instead of the usual platinum point projecting from an insulating tube within the liquid, there is here merely a platinum wire (*C*) dipping into the surface
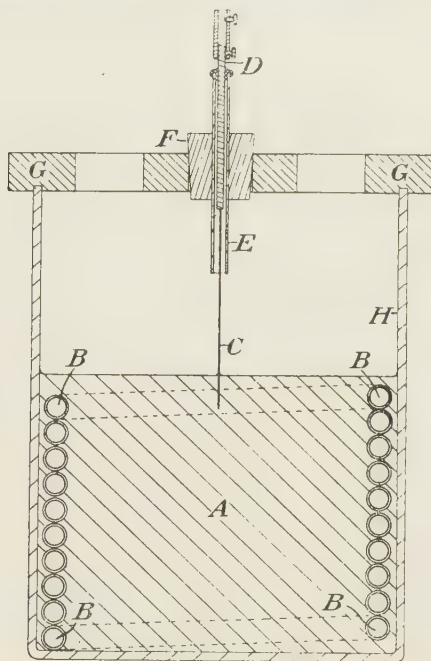
Fig. 5.—Improved Wehnelt Break.

of the electrolyte. The platinum wire is fused at its upper end into a stouter aluminium wire (*D*), sealed into a glass tube (*E*). The latter protects the joint from acid spray, and also slides within the rubber cork (*F*), thus permitting variation in the depth of immersion of the platinum wire. The length of wire immersed provides an admirable means of regulating the strength of the current, acting, presumably, as a variable resistance. It was, in fact, found possible to dispense with any additional resistance in the primary circuit. Phosphoric acid has apparently a higher specific resistance than sulphuric acid.* The apertures in the wooden lid (*G*) permit the escape of evolved gas.

At a later stage, an alternating current of 5 amperes at 70 volts and 50 cycles was passed through the primary of the induction coil, instead of using the Wehnelt

* F. H. Newman, Proc. Roy. Soc., 99, pp. 324-30 (1921).

break. It was found that for large currents the Wehnelt was apt to " kick " on occasion, the resulting surge in the secondary giving rise to minute sparks along the edges of the metal contacts in the sealing-wax rings, thus destroying the conductivity of any metal film sputtered across them.

General Notes.

A few observations made should be noted before passing on to the more tangible results attained.

The inclusion of a thermionic rectifier in the secondary circuit is desirable. Without one, it was found impossible to exceed a unidirectional current of 4 milliamperes in the secondary. The inclusion of a rectifier, however, results in a secondary current proportional to the immersion of the platinum wire in the electrolyte of the Wehnelt break. Again, without the rectifier, the anode of the bell-jar will be acting during part of the time of discharge as a kathode, not only lengthening the total time of sputtering required (for two reasons), but also tending to contaminate the kathode with deposits from the component metals of which the anode may be composed. A contaminated kathode can only result in a film of poor quality. Similar effects have been noticed elsewhere.*

The effect of the discharge on the collodion films to be sputtered is interesting. It is noticed that after the deposit has been made the films become somewhat flaccid, the part actually coated often developing corrugations. If this same film be again subjected to the discharge, the slackness and corrugations are taken up, the film becoming quite taut. It appears, therefore, that the discharge has the effect of tightening up collodion films, and it is not, therefore, surprising that non-flexible films shatter under the process.

With high orders of vacua, corresponding to a dark space of 2 in. and more, these films are thrown into violent vibration by the discharge. Continued exposure will, in fact, result in the fracture of the film.

Temperature Coefficients of Resistance.

As stated previously, it was necessary to deposit on the collodion films a metal which, in the sputtered condition, would have a maximum temperature coefficient of resistance.

Of the various metals sputtered, a good number were abandoned for purely negative reasons. In some cases the metal films were too thin or non-existant. In others sputtered films, otherwise satisfactory, failed to make contact with the metal insets provided for the purpose in the insulating ring supporting the collodion film. In the case of silver, for example, contact is apparently impossible on brass, but readily obtained on nickel.

Of the metals which gave satisfactory conducting films, two methods were used to determine the temperature coefficients, the first adopted being fairly accurate, but slow ; a later method, a rapid one, giving approximate results only.

Dealing with the latter first, it will be sufficient to state that it consisted in exposing the metal film to radiation from a focus lamp at a fixed distance. Given the numerical value of the temperature coefficient of resistance of one of the metals so tested, approximate values can be assigned to the others. Metals tested in this way, and their respective temperature coefficients, follow ; the values given depend-

---

* L. F. Curtiss, Phys. Rev., **15**, No. 6, III (1920).

ing on that found for bismuth, which was determined by the alternative method described later.

TABLE B.

Metal.			Change of resistance with standard illumination.	Calculated temperature coefficients of resistance.	Notes.
Bi	...	...	...	0·273 per cent.	−0·0011	(B)
Pb	...	...	...	0·43 ,,	+0·0018	(B)
Tl	...	...	...	0·3 ,,	0·0012	(A) through glass plate
14 Bi 1 Sn		...	0·24 ,,	−0·0010	(B)
Cu	...	...	...	0·07 ,,	0·0003	(A)
Ag	...	...	...	0·05 ,,	−0·0002	(A)
Pd	...	...	...	zero	zero	(B)
Ir	...	...	...	...	...	(A)
Ni	...	...	...	...	...	(B)

NOTES : (A) signifies film unblackened ; (B) blackened.

With the exception of bismuth, values of the above temperature coefficients do **not** appear in previous work. Those given above, of course, are very approximate
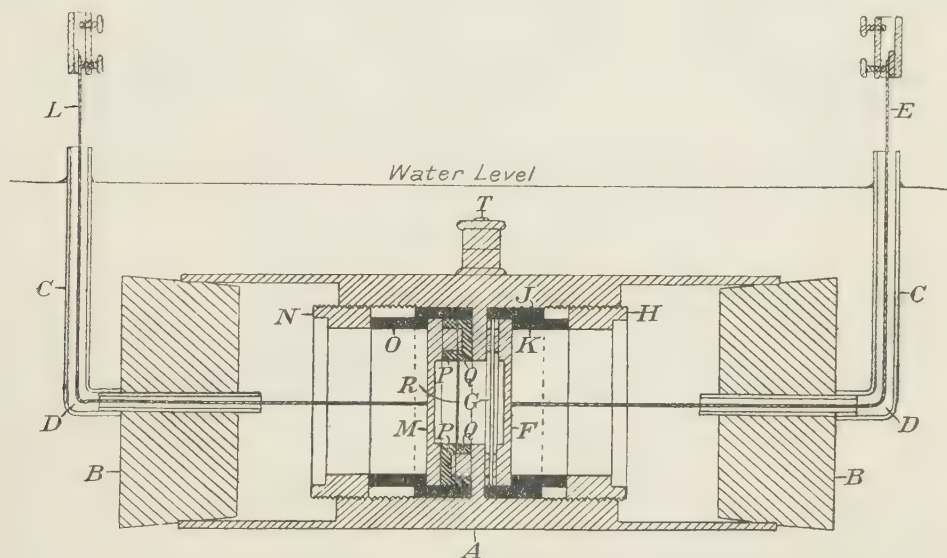
FIG. 6.—APPARATUS FOR DETERMINING TEMPERATURE COEFFICIENTS OF RESISTANCE.

only, and should be regarded as giving merely the order of the true coefficients in each case.

Apparatus.

The apparatus used for a closer estimation of temperature coefficients is shown, in section, Fig. 6. This consists of a brass tube (*A*), closed at each end by large rubber corks (*B*) (*B*), through which pass glass tubes. Attached to the outside end

of each glass tube are rubber tubes (C) (C).   Passing through these tubes are stout copper wires, which can be bent at the points D D to the shape shown.   To insert the various components, the copper wires are bent straight at D D, the corks and tubes being slipped off.   The whole apparatus being immersed in water to the level indicated, it is clear that the liquid is excluded from the interior, although the latter is in communication with the atmosphere.   One of the copper wires (E) is soldered to a brass disc (F), which is pressed into contact with one side of a platinum resistance thermometer (G) by the screwed brass ring (H).   This " thermometer " is merely the business part of a hot-wire microphone,* and consists of an annular disc of mica across whose centre is stretched a grid of very fine platinum wire, roughly 0.0015 cms. in diameter.   Contacts are made by two annular discs of tin-foil, one on each side of the mica.   Thus, the wire E is in electrical connection with one end of the thermometer grid G, whilst the other end is connected to the brass casing (A).   Insulation, where required, is provided by ebonite tubes (J) (K), the latter taking the pressure from the brass ring H.   On the other side, the copper wire L is soldered to a brass disc (M), which is pressed, by means of the screwed brass ring N and the in-

Bottom   Top   Bottom
(A)   (A and B)   (B)
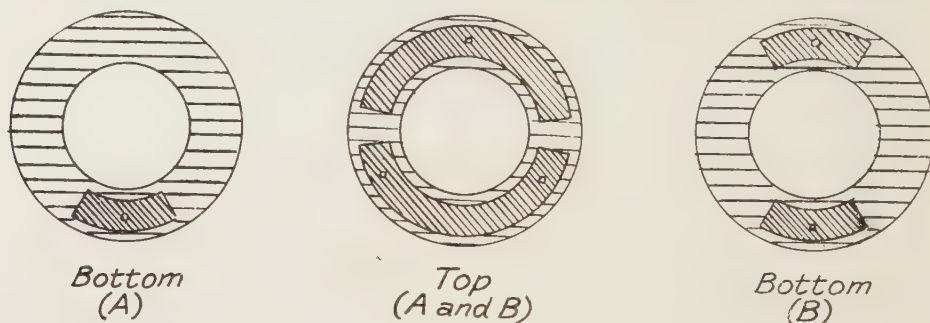
FIG. 7.—THE CONTACT RINGS.

sulating ebonite tube O, into contact with a sealing-wax contact disc (P), constructed as described later and shown in Fig. 7A.   This contact disc is identical in construction with those used for supporting the finished sputtered films.   One of the latter $(Q,$ Fig. 6) is in contact with disc P, the sides shown in Fig. 7 (top) being face to face. The other side of Q (Fig. 6), containing one contact, is pressed against the brass casing.   By this means one end of the sputtered bolometer strip (R) is in electrical contact with the wire L, whilst the other end is in connection with the casing (A). Again, the bolometer (R) and the thermometer grid (G) are near each other, and enclosed by blackened metallic masses in close proximity.   If the water surrounding the apparatus be raised in temperature, heat will be conducted through the walls of the brass tube A and radiated to the bolometer strip and the thermometer grid. Owing to the tenuity of both, they will each respond almost instantaneously to changes in temperature of the enclosure walls.   The experimental procedure is now clear.   The bolometer strip is included in one arm of a Callendar bridge by means of wire L and the common terminal T, whilst the thermometer grid is connected up in a second bridge of this type by the wire E and terminal T.   The apparatus being

* W. S. Tucker and E. T. Paris, Phil. Trans, A, Vol. 221, pp. 389-430.

immersed in melting ice, the resistance of both the bolometer and thermometer are measured. The ice-and-water bath is fitted with two mechanical stirrers. The stirring must be really efficient, and in these experiments the two stirrers were so arranged that water was continuously rotating round the brass tube at a fast rate. The bath is now heated at a uniform speed up to about 30°C., and parallel resistance readings taken on each bridge at intervals of one-half to one minute. Although the temperature of the blackened enclosure may lag behind that of the water bath by several degrees, yet the temperature of the bolometer and thermometer will always be that of the enclosure, and therefore the same at any given instant. If any assumptions are made here, their justification appears in the results obtained.* Three metals were tested in this manner (platinum, gold and bismuth), the resistance temperature curves being given in Figs. 8, 9 and 10. They are all straight lines within the limits of experimental errors. That for bismuth is especially interesting in that two curves are given relating to two different specimens. The curves are parallel, and the coefficients therefore the same, within the limits of experimental error, although their resistances at 0°C. are different. It would appear probable, then, that the resistance and age of a sputtered film have little or no effect on the temperature coefficient.†

The coefficients obtained were :—

TABLE C.

Metal.	Resistance at 0°C.	Temperature coefficient.	Temperature coefficient of metal in bulk.	Ratio of coefficients.
Pt	477·8 ω	+0·000040	0·0038	1/95
Au	28·54 ω	+0·00072	0·0040	1/5·5
Bi	1430·0 ω	−0·00110	0·0042	1/3·8
Bi	1399·0 ω	−0·00112	...	...

that for gold not having been previously determined elsewhere. Those for platinum and bismuth compare with values obtained by other workers as follows :—

TABLE D.

Metal.	Temperature coefficients found.	Becker and Curtiss.‡	Richtmyer & Curtiss.	Koller.§	Reynolds.¶
Pt ...	+0·000040	...	...	From small negative up to +0·002	From small negative up to +0·003
Bi ...	−0·0011	−0·001 to −0·003	−0·0016 to −0·0029	...	...

* The lag in all experiments was 9·4°C., and was constant within one-half of 1 per cent.
† Cf. F. K. Richtmyer and L. F. Curtiss, Phys. Rev., **15**, No. 6, II (1920).
‡ J. A. Becker and L. F. Curtiss, Phys. Rev., 15, No. 6 (1920).
§ L. R. Koller, ibid.
‖ F. K. Richtmyer and L. F. Curtiss, loc. cit., ibid.
¶ F. W. Reynolds, Phys. Rev., 24, pp. 523-31 (1924).
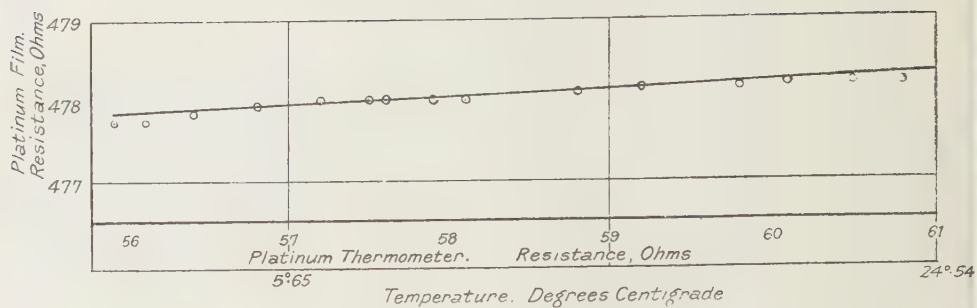
FIG. 8.—TEMPERATURE-RESISTANCE CURVE FOR PLATINUM.
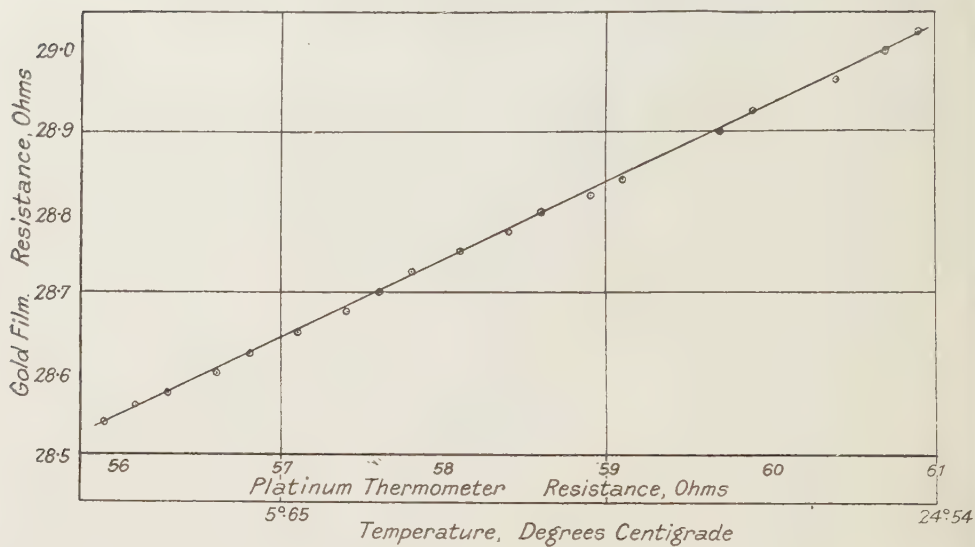
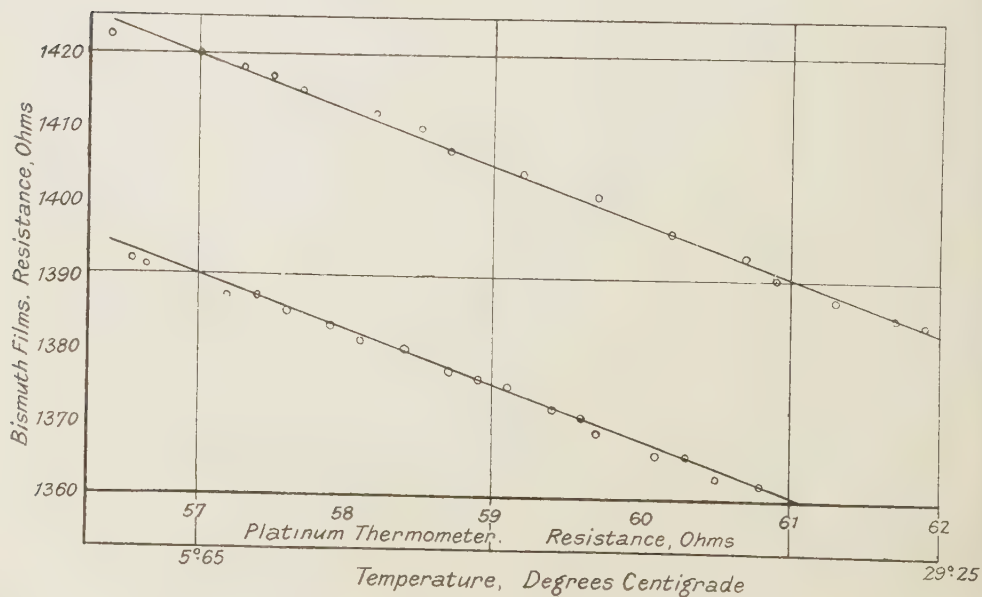FIG. 9.—TEMPERATURE-RESISTANCE CURVE FOR GOLD.

FIG. 10.—TEMPERATURE-RESISTANCE CURVES FOR BISMUTH.

In the case of bismuth the coefficient determined comes within the ranges quoted by others. For platinum, although only one result is quoted, a number of films were tested roughly, and in all cases a very small positive coefficient was found. Koller obtains his high positive coefficients by ageing at 200°C., whereas his unaged very thin films have negative coefficients. Reynolds observes the same, and attributes the reversal of the coefficient to absorption of oxygen whilst hot, as heat ageing alone is insufficient.

The new coefficient quoted for gold is probably reliable in cases where heat or chemical ageing has not taken place, a number of films roughly tested giving the same result.

It appears, therefore, that the four metals with the greatest temperature coefficients are :—

Lead	...	...	...	...	...	+0·0018 (approx.)
Thallium...	...	...	...	...	0·0012 (estimated)
Bismuth ...	...	...	...	...	−0·0011
Gold	...	...	...	...	...	+0·00072

Bismuth has, so far, been chosen as the metal to be used in the construction of these bolometers, as both lead and thallium oxidise in air, the latter with remarkable rapidity. Even when enclosed in a vacuum of a fraction of a millimetre of mercury of air, a film of thallium is completely oxidised in four days. Experiments are being made, however, with a view to constructing bolometers of lead and thallium enclosed in inert gases at low pressures.

Ageing.

The temperature coefficients of resistance should be considered in connection with the specific resistance of the film and its previous history. With regard to the latter, any process of ageing through which the film may have passed is important. Of the causes of ageing, possibly that of heat and that of time (atmospheric and inter-molecular action) show the greatest effects. No definite experiments were undertaken to determine these effects, but some data were incidentally obtained which may prove of interest.

Before being used as bolometers, the thin metal films obtained were blackened by smoking over a flame, a rise in temperature being thus involved. In every case a change of resistance was noted. These are tabulated below.

Metal.	Resistance.	Change.
Ni	579 ω	+ 0·5 ω
Pb	240 ω	+ 55·0 ω
Pd	3,280 ω	+ 474·0 ω
Bi	2,692 ω	+ 186·0 ω
Bi	4,500 ω	+ 735·0 ω
Bi	6,190 ω	+2,980·0 ω

The rise in resistance on heating in the case of nickel is remarkably small, amounting almost to constancy in resistance on heating. The three cases quoted for bismuth tend to show that a greater rise in proportion to the original resistance takes place the higher this initial resistance may be. Of the above, bismuth only figures in previous work, Richtmyer and Curtiss having dealt with this increase in the resistance of bismuth on heating in air.

A table follows giving the increases in resistance of various films acquired on being left in air for several days.

Metal.	Resistance.	Change.	Time.
Au	28·75 ω	+ 0·025 ω	1 day.
Pb	295·2 ω	+ 716·0 ω	4 days.
Ag	1,260·0 ω	− 13·0 ω	10 ,,
Bi	1,058·0 ω	+ 229·0 ω	6 ,,
Bi	1,370·0 ω	+ 377·0 ω	6 ,,
Bi	5,235·0 ω	+2,365·0 ω	14 ,,

Here gold displays a very small increase, but silver* is unique in showing an actual decrease. The three cases of bismuth, as in the case of heat ageing, seem to show an increase in resistance out of proportion to the original resistances. In this connection, the curves shown in Figs. 11 and 12 are not without interest. They

FIG. 11.   FIG. 12.
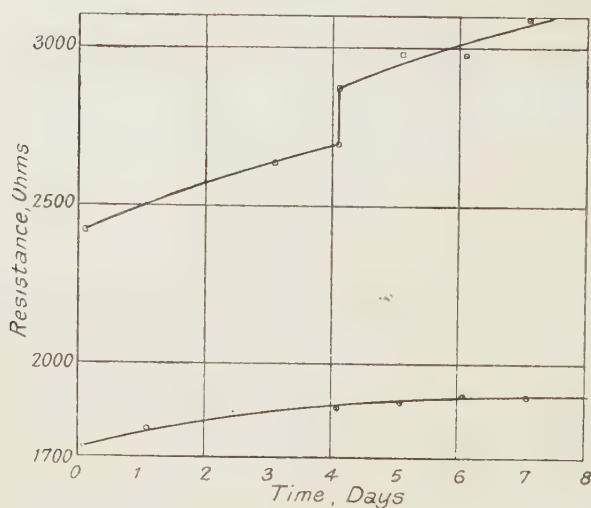
RESISTANCE : TIME CURVES FOR BISMUTH.
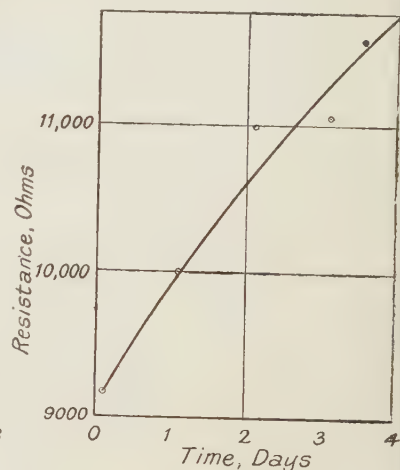
relate to three other specimens of bismuth and show that the resistance does not increase linearly with time, but tends to a practical limit.† It also would appear that the curves are steeper, the greater the original resistance, confirming the deduction from the three cases of bismuth in the table just given. The break in the second curve, Fig. 11, is due to heat ageing —the film having been blackened at this point. The increased steepness in the resistance-time curve with the increase in " original " resistance is very striking.

Ageing with time in air does not appear to have received a great deal of attention. The practical limit for ageing in air, in the case of platinum, found by Koller, is attributed by him to adsorption of air, hydrogen or oxygen.

* Cf. decrease with heat ageing.   J. Patterson, Phil. Mag., 6, 4, p. 652 (1902).
† Cf. case of platinum.   L. R. Koller, loc. cit.

Resistances.

The resistance of a bolometer film of the size used ($\frac{1}{4} \times \frac{3}{4}$ inch) varies, of course, with the meta of which it is made. It is interesting to compare these, although, owing to variations in thickness, it may occasion surprise that one should associate any definite resistance with a particular metal. It is found, however, that there appears to be, when considered from the view-point of its ultimate purpose, an optimum range of resistance (possibly associated with a particular range of thicknesses) for each metal. Below are given examples of resistances possessed by various metals, sputtered under similar conditions, which may give some idea of the order of resistance that can be expected for any particular metal.

Metal.	Resistance.
Au	60 ohms.
Pb	270 ,,
Cu	470 ,,
Tl	310 ,,
Pd	3,200 ,,
Ir	3,600 ,,
Ni	580 ,,
Ag	1,300 ,,
Pt	270 ,,
Bi	2,010 ,,

These resistances are representative only of films immediately after sputtering.

Improved Sputtering Apparatus.

At this stage, the need for a sputtering apparatus of greater versatility became apparent. Improvements and additional facilities were needed in the following : (1) A bell-jar is needlessly large in view of the smallness of the area required to be sputtered, and involves longer periods of evacuation. (2) The separation of the bell-jar from the base-plate after sputtering, in order to remove the films, is difficult owing to the large area of contact. The wax joint has invariably to be warmed prior to breaking. (3) Provision should be made to fill the apparatus with gases other than air. (4) In the apparatus already described it is necessary on completion of sputtering to remove the film from the bell-jar (after admitting air), and to mount it in some type of holder providing electrical contacts, before its resistance and temperature coefficient of resistance can be measured. Apart from possible oxidisation of the film, this procedure is a delicate one fraught with numerous possibilities of accident to the fragile films. It would be an advantage, therefore, if the ring supporting the collodion film were already mounted in a holder providing electrical contacts to the outside of the apparatus before subjection to sputtering. In this way, the resistance of the film may be measured without breaking the vacuum. Not only this, but continuous readings of the resistance could be made during the whole process of sputtering. (5) If the apparatus can be so arranged that a beam of radiant heat be directed on to the film, an estimation of the temperature coefficient of resistance is possible at any stage of manufacture. (6) In the case of metals oxidisable in air, or more freely sputtered in other gases, it would be necessary to remove the sputtered film in its holder rendered gas-tight, by some device or other, before admitting air to the apparatus. In other words, the bolometer should be capable of being " bottled " in vacuo. (7) Owing to the fact that the supporting

rings are made of sealing-wax and there is a definite heating effect associated with the discharge, some form of cooling is necessary to prevent distortion of these rings.

All these improvements are effected in the apparatus shown in section, Fig. 13. This consists essentially of a cylinder of glass (*A*), ground flat at each end, on which fit two aluminium shoulder-pieces (*B*) (*C*) of such a shape that distortion due to atmospheric pressure (and consequent fracture of the joints) is reduced to a minimum. The top piece (*B*) carries at its centre a circular disc of rock-salt (*D*) with optically worked faces. There are, in addition, two glass tubes fitted with taps (one only shown, *E*), and a ground-glass joint carrying the aluminium kathode lead
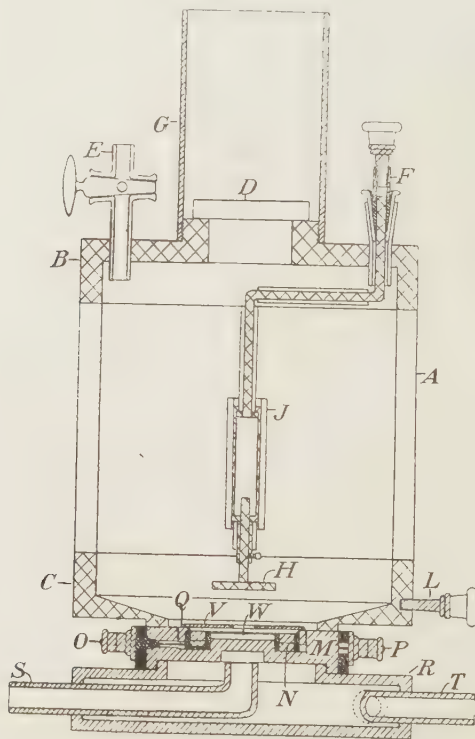
Fig. 13.—Improved Sputtering Apparatus.

(*F*), the inner member of which is capable of rotation about a vertical axis. Screwed round the rock-salt disc is a brass tube (*G*), on which can be fitted the standard source of radiant heat (a Nernst lamp—not shown) when required. The kathode lead (*F*) ends in a rectangular slab of the metal to be sputtered (*H*), and, together with the modification (*J*), the purpose of which is described later, is clothed in glass tubing. It will be seen that a partial rotation of the ground-glass joint at *F* will remove the kathode from over the central orifice in (*C*) to the side, where a preliminary sputter can be made to clean the kathode. The whole of the aluminium base (*C*) can be made the anode by fitting the conducting-plug (*L*). Beneath the base-plate is attached the film-holder (*M*) (also shown separately in Fig. 21). This holder, when removed, constitutes the complete bolometer itself, as will be shown. There is only one aperture to this holder which, when in the position drawn, is totally within

the apparatus, and is therefore gas-tight. Inside the holder at N (Fig. 13) is a sealing-wax contact-ring (Fig. 7A), with two contacts on top and one beneath, the latter making contact with the body of the holder. The other contact, which only occupies a part of the depth of the ring, is connected by means of an insulated wire to the terminal O (Fig. 13), the aperture in the holder through which the wire passes being rendered air-tight by a conical plug of " Chatterton's " compound. The terminal (P) is in contact with the body of the holder. The sealing-wax ring, with a collodion film stretched across its aperture, is placed on top of the contact-ring (N), and screwed down by the brass ring (Q). This film-supporting ring is modified, as shown in Fig. 7B, in that it has two contacts on each face, the top pair providing contacts for the sputtered metal film, whilst the lower pair make contact with those of the ring below. When the metal film-strip has been sputtered on to the collodion film and its supporting ring, it is obvious that one end will be in connection with terminal O (Fig. 13), and the other end to P, both terminals being outside the apparatus. Screwed into the base of the film-holder (M) is the water-cooling jacket (R) with its supply pipes arranged so that the jacket is always full of water and the exit pipe (S) so placed that adequate cooling is ensured to the base of the film-holder. The entry pipe (T) is bent at right-angles inside to give the water a rotary motion within the jacket. By this means the sealing-wax rings above are kept efficiently cool by conduction.

All joints in the apparatus described are rendered air-tight by means of soft-wax tapes. The liquid-air apparatus, similar to that shown fixed to the bell-jar in Fig. 3 is here kept separate, connection being made by means of rubber pressure-tubing to one of the glass taps fitted to the top. In this way the sputtering apparatus can be turned upside down when required without reversing the liquid-air tubes.

With this instrument the resistance of the sputtered film can be measured continuously during its manufacture by connecting the terminals O and P (Fig. 13) in series with a cell of known E.M.F. and a micro-ammeter with shunts (calibrated, if desired, direct in ohms). At any period during its formation, the temperature coefficient of resistance of the sputtered metal can be measured by rotating the kathode (FJH) clear of the film, and attaching the Nernst lamp to the tube G on top of the instrument.

The volume of air to be evacuated in this apparatus is much smaller than in the previous bell-jar. The joint to be broken (that between the base-plate (C) and the film-holder (M)) is so much smaller that preliminary heating of the wax is unnecessary, and makes for economy in wax. Being fitted with two taps, it is possible to fill the apparatus with any gas desired.

In the case of a metal film which is adversely affected by air, it is possible to bottle it in vacuo by an auxiliary apparatus (not shown), containing a rock-salt disc at one side, interposed between the base-plate and the film-holder. On the completion of sputtering, the whole apparatus is inverted and a subsequent tilting slides the disc into position immediately beneath the film-holder. By again placing the apparatus in an upright position, the rock-salt disc will fall into position over the aperture in the film-holder (surrounded, before evacuation, by a thread of soft wax). Admission of atmospheric pressure to the apparatus forces the disc into contact, effectively sealing the film-holder from the atmosphere. The holder can then be removed and forms a complete air-tight bolometer. The reason for the

modification in the design of the kathode at J is now clear. Owing to the thickness (about $\frac{1}{2}$ inch) of the subsidiary apparatus inserted between the base and the film-holder the kathode will normally project somewhat into the centre of this auxiliary apparatus. On reversing, however, the modification in the kathode is automatically shortened by gravity, and clears the central space sufficiently to allow the rock-salt disc to be slid into position. Normally the mask which controlls the shape of the sputtered film is located, as shown, at V. When, however, the subsidiary apparatus is in use the mask is placed inside the latter, and is swung clear when the rock-salt disc slides into position.

In some cases the film-holder itself was made the anode instead of the base-plate by interposing a thin ebonite washer between C and M, and making terminal P the anode. This always accentuated a peculiar phenomenon noted in all cases—viz., a subsidiary current, due to the discharge, set up in the circuit connected to the terminals O and P for measuring the resistance of the sputtered film. This
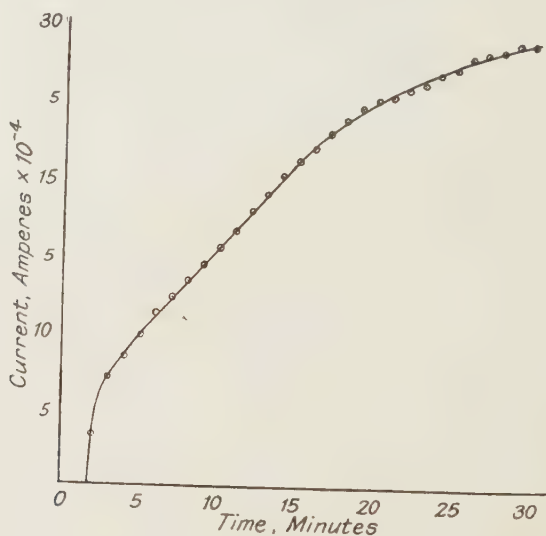
FIG. 14.—GROWTH OF A SPUTTERED FILM.

current is due, of course, to an E.M.F. set up on the film-contacts, owing to an asymmetric kathode-fall of potential between the electrodes. This is very marked when the rectangular kathode is so placed that it is not truly parallel to the mask aperture. It is usually made visible by the anode glow on the contacts, the glow disappearing when true parallelity is attained. As an example, a current, due to the discharge, of 150 micro-amperes was reduced to 7 micro-amperes with correct adjustment. In all cases, too, this discharge-current is increased when the water-cooling is used, the increase being of the order of 10 times. This is possibly due to inefficient insulation from the earth of the coil and other apparatus used in producing the discharge. In any case, however, the anode glow disappears, together with the " discharge-current," on increasing the vacuum (say, of that associated with a dark-space of 1·5 cm.).

With this new sputtering apparatus an interesting result has been obtained,

throwing some light, perhaps, on the process of sputtering. The curve in Fig. 14 shows the increase of current through the film (a criterion of its decreasing resistance) against time of sputtering. The curve (for bismuth) seems to be made up of three parts, of which the middle part is approximately a straight line. The first part, curved, can be explained if we imagine that the film has been sputtered in part before contact begins to be made. Contact will occur suddenly some time after commencement of sputtering and will become more and more widespread as an ever increasing number of linkages are made between the various aggregations of sputtered particles. After a time contact is " perfect " throughout, and the straight second part of the curve shows conductivity as strictly proportional to thickness. The third curved portion is more difficult of explanation. When it is known that frequently at the end of such a curve conductivity often ceases quite suddenly, a reasonable supposition is that the aggregation of molecules, after a certain thickness is attained, is accelerated ; the aggregations eventually becoming large enough to split the film across, although such splitting may be quite invisible. This " ageing " may be due, of course, to the higher temperature, derived from the discharge, which would be attained with a greater thickness. Herein lies the basis for the previous statement that there is a range of optimum resistance for each metal ;
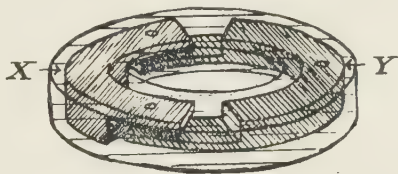
FIG. 15.—SKELETON VIEW OF A CONTACT RING.

this range coinciding, one would say, with the straight portion of its characteristic curve.

It has been repeatedly noticed that if attempts are made to obtain much thicker deposits of low resistance by protracted sputtering, conductivity ceases suddenly soon after the optimum resistance has been attained, but will build up again and again to the same value. In the case of bismuth, for example, it seems impossible to obtain a permanent film of less than 1,500-2,000 ohms.

III. On the Construction and Performance of the New-type Bolometer.

General Construction.

A description of the component parts of the bolometer follows. The process by which the necessary thin collodion films were made, and the method of coating these with thin films of metal by sputtering, have already been described.

To support the thin collodion film, a flat annulus of sealing-wax is used, inset with metallic contacts. These are shown in plan, top and bottom, in Fig. 7 ; also in skeleton, Fig. 15. The collodion film adheres to the top of the ring ; thus there are, beneath the film, two wide contacts, one for each end of the metallic overlying strip subsequently sputtered. In one type of ring there is one contact only going through to the bottom (Fig. 7A) ; in the other, both go through (Fig. 7B).

Moulding Apparatus for Contact-rings.

The apparatus used to make these rings is shown in Fig. 16. This consists of a flat, circular vessel, composed of a base-plate (*A*) and a rim (*B*), split into two semi-circular halves, all of brass. This vessel rests in a circular depression in an iron plate (*C*) fitted with two upright iron guide-rods. Sliding on these rods is a bridge (*D*), carrying the mould (*E*). The brass contact-pieces, shaped as shown in skeleton below, are screwed on to the base-plate (*A*) by means of four screws. The first (*F*) secures the bottom part of contact *X* flush against the base-plate, whilst the second (*G*) has the top end of its thread turned off to form a collar, the latter holding contact *Y* 1-32nd of an inch from the base-plate. (In the case of rings of type *B*, Fig. 7, contact *Y* and its associated screw are modified so that *Y* is in contact with the
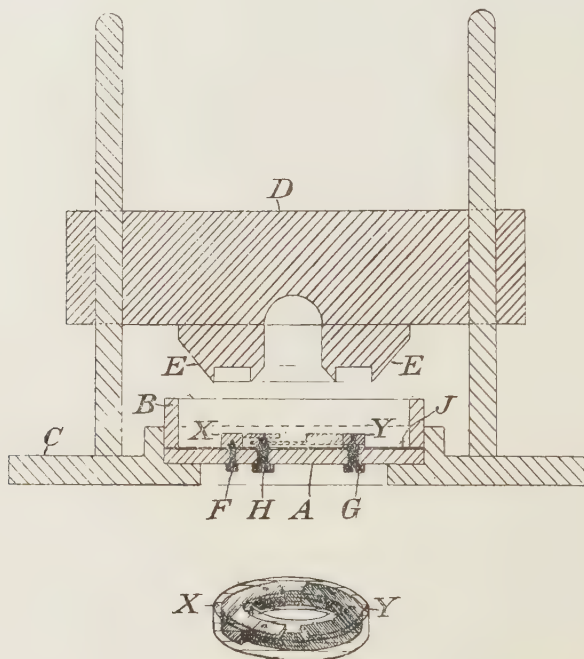
Fig. 16.—Moulding Apparatus for Contact Rings.

base-plate in order to give the second bottom contact.) There are two further screws (*H*), one of which is incorrectly shown, for the sake of clearness, in the plane of the section, both being turned off with the two collars of different diameters, which hold the laminated ends of the contacts *X* and *Y* 1-32nd of an inch apart. Interposed between the base-plate and the metal contacts is a very thin disc of asbestos paper (*J*), the purpose of which will appear immediately.

Process of Moulding.

The process of ring manufacture is very simple. The bridge and mould are removed, the remainder of the apparatus being heated to the temperature of melting sealing-wax. A small quantity of the molten wax is poured into the cavity, and when no further air bubbles appear and the wax smooth, the bridge and mould are

replaced and forced on to the wax in a press. In this way the wax is made to adhere to the metal contacts by reason of their high temperature, but not to the mould owing to its large mass of cold metal. Neither will the wax stick to the hot base-plate, owing to the interposition of the asbestos paper. When cold the mould is pulled away, the screws removed and the brass box (*A*, *B*) split apart, leaving a complete ring adhering to its asbestos paper. Both sides of the ring are rubbed down on fine glass paper until the paper is removed from the bottom and the contact faces, top and bottom, are flush with the surrounding wax. The contacts being quite level with the wax surface, the superimposed collodion film will overlie the junction without the formation of a ridge or gap. Consequently when the thin metal strip is sputtered across the whole from contact to contact there is no chance of continuity being broken at a " precipitous " junction of metal and wax.

The Contact Rings.

The appearance of the finished ring is shown in plan in Fig. 17. Here *A* is the wax ring, *B* and *C* the metal contacts. A collodion film (*D*) is superimposed and its periphery removed by wiping with alcohol so that it just covers the aperature of the ring and the junction between the metal and wax, leaving the majority of the metal contact surface exposed, ready to receive the ends of the sputtered bolometer
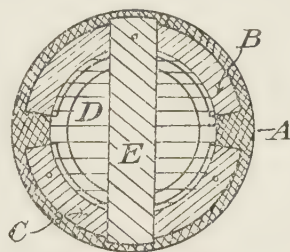
FIG. 17.—DIAGRAMMATIC SKETCH OF A FILM BOLOMETER.

strip (*E*). It is clear that the latter will be in electrical contact at its ends with *B* and *C* and yet will be practically flat throughout. The only possible deviation from the horizontal will be at the boundary of the collodion film. As, however, the film is " shelved " off owing to the action of the alcohol, and in any case its thickness is of the same order as that of the bolometer strip, it is found that the method provides a certain and perfect contact. In the diagram, portions covered by others are shown unshaded.

It should be noted in passing that the overlapping of the laminated ends of the metal contacts within the enclosing wax augments the mechanical strength of the rings. So much so, that they may be dropped on the floor without fracture, whereas without the overlap the rings are almost too brittle to be handled.

The metal inset contacts were made of brass, nickel and steel. The steel contacts are most satisfactory from the point of view of oxidisation, provided that they are kept reasonably free from moisture.

Blackening.

For use in air, these bolometers have now to be blackened—the sputtered strip possessing normally a mirror-like surface. Blackening is carried out by means of the apparatus shown in Fig. 18, the purpose of which is to provide finely-divided

smoke at a temperature sufficiently low to obviate destruction of the collodion film. Smoke is obtained by means of the paraffin lamp (*A*) providing a small, smoky flame. This rises up through the bell-mouthed metal chimney (*B*), taking with it a large quantity of air. Over the aperture of the chimney is a metal disc pierced at its centre with a small hole. The disc is held clear of the chimney top by two pieces
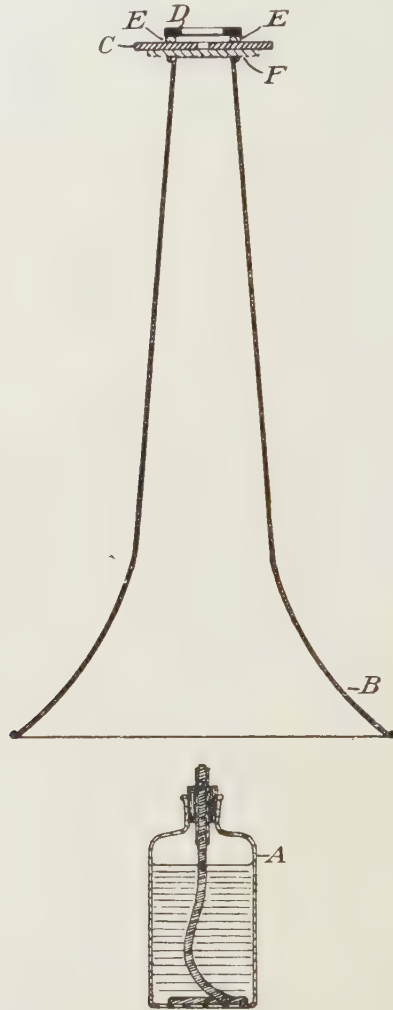

Fig. 18.—Apparatus used for Blackening Film Bolometers.

of wood (*F*) and supports, in its turn, spaced in the same way by two further pieces (*E, E*), the wax ring carrying the metal film to be sputtered facing downwards. Smoke will be rble to escape from under the disc (*C*), but a small quantity of cooler smoke will pass through the hole, playing on the film surface ; part being deposited, the remainder escaping from underneath.

The finished bolometer, when smoked, is mounted in the holder shown in Fig. 19. This consists of a brass cylinder (A), covered with an ebonite sleeve (B). Inside, at the centre, is an ebonite cylinder (C), fitted in the middle with an ebonite disc (D). Adjacent to this disc is another of brass (E), against which presses the bottom face of the ring carrying the bolometer film (H), its one contact on this side (F) connecting electrically to the disc (E). Pressing against the top surface of this
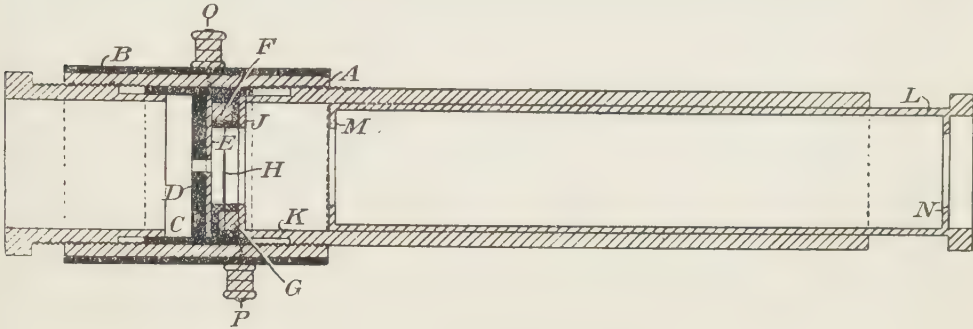
FIG. 19.—HOLDER FOR FILM BOLOMETER.

ring is a second ring of the same type (Fig. 7, A), the two top faces being in contact. The contact coming through to the bottom (G, Fig. 19) connects to the brass washer J, the whole being pressed into intimate contact by the screwed tube K. From the two brass discs E and J wires pass to the terminals O and P through insulated slots (not shown) in the body of the tube A. One end of the bolometer strip will thus be connected to the terminal O and the other end to terminal P. Air draughts are excluded by the tube L, sliding within K, which carries two baffles at M and N, the shape of the apertures being rectangular, similar to that of the bolometer strip.
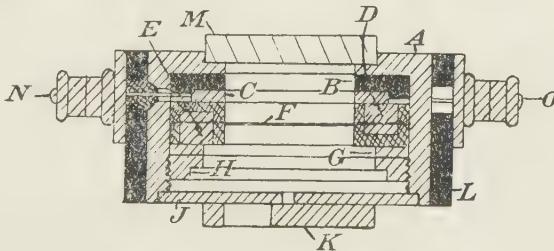

FIG. 20.—GAS-TIGHT HOLDER.

The discs D and E are pierced with apertures at their centres in order that the bolometer may be alined on to any source of heat by sight.

In cases where the bolometer films are to be kept from contact with the air, the gastight holder shown in Fig. 20 is used. Here exactly the same method of mounting is observed as in the air type above, with the exception that the casing is used as one terminal (O). The other terminal (N) is connected to the contact washer (C) by means of a wire passing through the casing, the aperture being sealed with " Chatterton's compound." The top of the holder is sealed with a rock-salt disc (M),

the joint being made with wax tape. The bottom is sealed by a brass disc (*J*), waxed at the rim, pierced with a small hole at the centre. Sliding over the disc, on a film of soft wax, is another thicker one (*K*), with a much larger hole placed eccentrically as shown. The bolometer having been made and mounted up inside, the disc *J* is waxed on and the second disc (*K*) placed in position with its aperture over that in *J*. The end of a glass tube, connected to an air pump, is inserted in the aperture of *K* and waxed in, the holder then being evacuated. Sealing under vacuo is effected by sliding the disc *K*, slightly warmed, until the apertures no longer coincide. The glass tube can then be removed, leaving the bolometer mounted ready for use in vacuo.

The two types of holder described above are for use in the case of those films made in the bell-jar apparatus (Fig. 3).

The third type (Fig. 21) is a component part of the improved sputtering apparatus (Fig. 13), and forms a complete holder to the interior of which air need never be admitted. The connections have already been described. The one aperture is sealed by the rock-salt disc *J* (Fig. 21). It should be noted that the film surface is within 1/32nd of an inch of the top of the holder, this form of construction being expedient owing to the fact that the mask (placed of necessity on top of the holder)
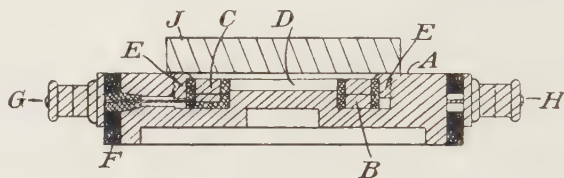

FIG. 21.—VACUUM HOLDER.

must be very close to the film to ensure a clean image of its aperture being thrown in sputtering.

The Bolometer in Use.

The intention in designing the new type was that of reducing, still further than in existing types, the thickness of the bolometer grid. It should be remembered that one may sputter an almost impalpable metal film, the only restriction being that it must conduct an electric current. Practically transparent metal films could therefore be used. One is handicapped, however, by the need of a supporting film of some insulating substance ; and, speaking generally, it is the combined thickness of the metal and supporting films together which will determine the lag of the instrument. Unless this combined thickness is less than that of the metal grids in other types, obtained by rolling or chemical means, the new type will show no advantage in the matter of speed of response.

Sensitivity.

Tests have shown that a definite advance in " speed " has been obtained, but with the sacrifice of a certain amount of sensitivity. In the case of the bismuth bolometer, for example, it will be remembered that in the sputtered condition bismuth has a temperature coefficient of resistance a little less than a third of that of platinum in bulk. It is possible that the lead type, with a coefficient of roughly a half, may
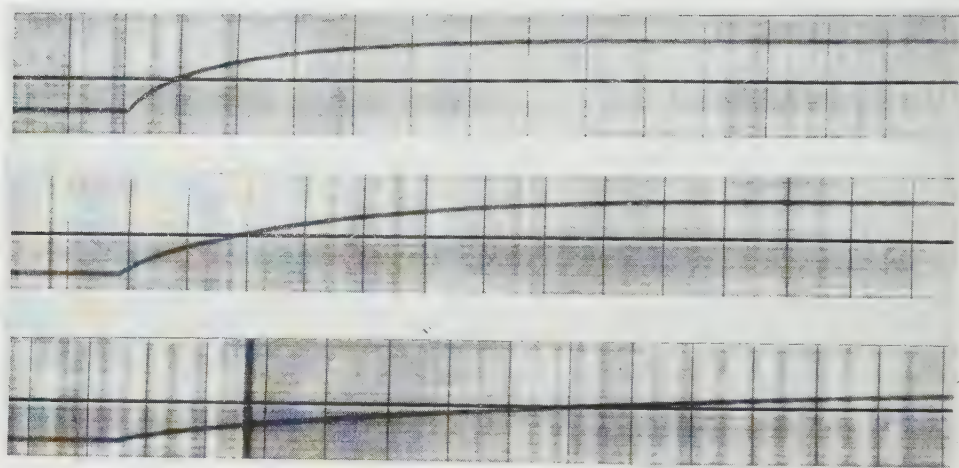
FIG. 22.—PHOTOGRAPHIC RECORD OF FASTER RESPONSE OF FILM BOLOMETERS (TOP PAIR).

prove better eventually, whilst thallium may show still better results. At the moment, however, we must accept the sensitivity of the new type as roughly a third of that of previous types (using platinum grids), *ceteris paribus*.

Sensitivity Data.

To determine the response of a film bolometer to radiation of known intensity, a focus lamp radiating 0·95 gm. calories/cm.²/min. was placed at a distance of 500 mms. The change in resistance having been measured, the Lummer and Kurlbaum* was substituted at the same distance.

Intensity of radiation.	Change of Resistance.	
	Film type.	L. & K.
10·56 milliwatts/cm.²	0·316 p.c.	1·07 p.c.

The ratio of sensitivity is therefore $\dfrac{L \& K}{\text{Film}} = 3.39$.

Speed.

To determine what advance had been gained in speed, comparative photographs were taken, using the Einthoven string galvanometer. Comparison was made with a Lummer and Kurlbaum bolometer,* which would appear to embody the greatest advances in speeding up these instruments by reduction of the grid thickness to the lowest possible mechanical limits.

A preliminary photograph was taken with the Einthoven to ensure that no extraneous mechanical or electrical vibrations were being recorded. A second film depicted the effect of a commutated current in a non-inductive circuit. Inspection of this photograph enabled one to estimate the natural frequency of vibration of the string itself, and to ensure that its period was of a different order to that expected in the response of the bolometers to heat impulses.

Time markings, perpendicular to the travel of the photographic film, were made every one-fifteenth of a second by an apparatus whose driving motor was controlled by a tuning-fork of known frequency, a stroboscopic attachment ensuring that the control was visibly effective. The galvanometer string was connected to a Wheatstone bridge containing the bolometer, and on the latter being exposed suddenly, by means of a " Compur " shutter, to a beam of radiant heat, the bridge is thrown out of balance and the change in resistance results in a lateral displacement of the string-shadow in the camera.

The motor drive for the film having been started, this apparatus would be brought into play, thus photographically recording the growth of the bolometer current due to exposure to a heat source from some definite starting moment up to the attainment of the full deflection.

Fig. 22 shows three actual photographs taken in this way, the bottom one due to the Lummer and Kurlbaum, whilst the upper pair refer to two different types of " film " bolometers. The equidistant parallel lines are the time marks, and give us time abscissæ ; whilst the distance between the film shadow and the straight line down the middle of the film gives ordinates of deflection. It will be seen that the

* Ann. der Physik, Bd. 46, p. 204 (1892).

response of both film bolometers is much quicker than that of our standard of comparison, especially in the case shown in the top photograph. The latter refers to the later type of instrument, previously mentioned, whose supporting collodion film is roughly one-half the thickness of that of the original specimen, of which the middle photograph is representative.

These photographs were measured up on a travelling microscope, the results being plotted as in Fig. 23. It was found that measurements of deflection could be repeated to within 1/50th of a millimetre, the full deflections ranging from 10 to 15 millimetres. The same accuracy was probable in the case of the time measurements. These orders of accuracy are in excess of possible experimental errors. As far as the timing was concerned, this was never further out than one beat in 180, so that an accuracy of 1 in 150 is certain. Two sources of error are possible in the
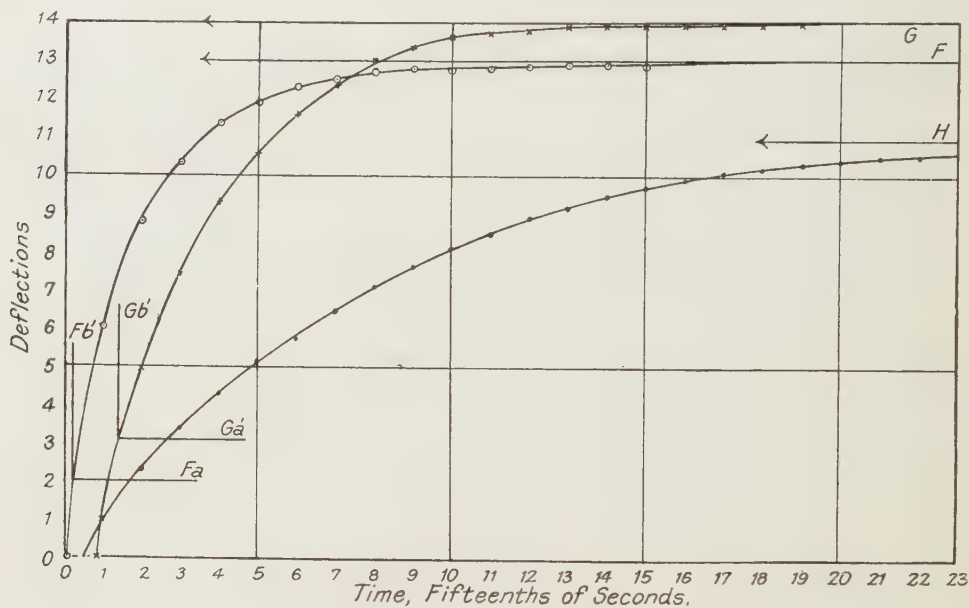

Fig. 23.—Response of Comparative Bolometers to Radiant Heat.

experimental recording of deflections. The first, which in view of the results may be neglected, is the possible distortion of the photographic film in the camera. The second, an irregular electrical vibration of the galvanometer string, occurred in some cases, and is due to fields set up by the electric arc used as an illuminant. In trial photographs of a commutated current, previously referred to, these irregularities are distinctly traceable to variations in the strength of the arc currents, as the latter are registered at varying periodic intervals parallel to the time markings, similar to those visible in the three photographs in Fig. 22. The two irregularities occur simultaneously. These displacements of the string shadow, due to extraneous causes, are of the order of 1/10th of a millimetre as a maximum. We shall therefore be justified in regarding our measurements of deflection as accurate only to 1 per cent. This inaccuracy, due to an illuminant unsuited to its purpose, could not be avoided, as no other was available ; most of the apparatus, as a matter of

fact, with the exception of the galvanometer itself, was made up in the laboratory. In passing, it should be remarked that the test film referred to showed that the galvanometer was practically dead-beat at the string tension used, the minute oscillations present dying down in less than 1/100ths of a second.

In Fig. 23, the faster type of film bolometer gives the graph F, the slower one G; H being due to the Lummer and Kurlbaum standard. It will be seen that each curve approaches its final deflection asymptotically, and each can be roughly represented by the formula

$$\theta = \theta_\infty (1 - e^{-at}),$$

where θ gives the deflection at any moment, θ_∞ is the final deflection, a is a constant and t the time.

It is a very difficult matter to arrange the apparatus so that each bolometer gives the same final deflection on the photographic film. To compare the perform-
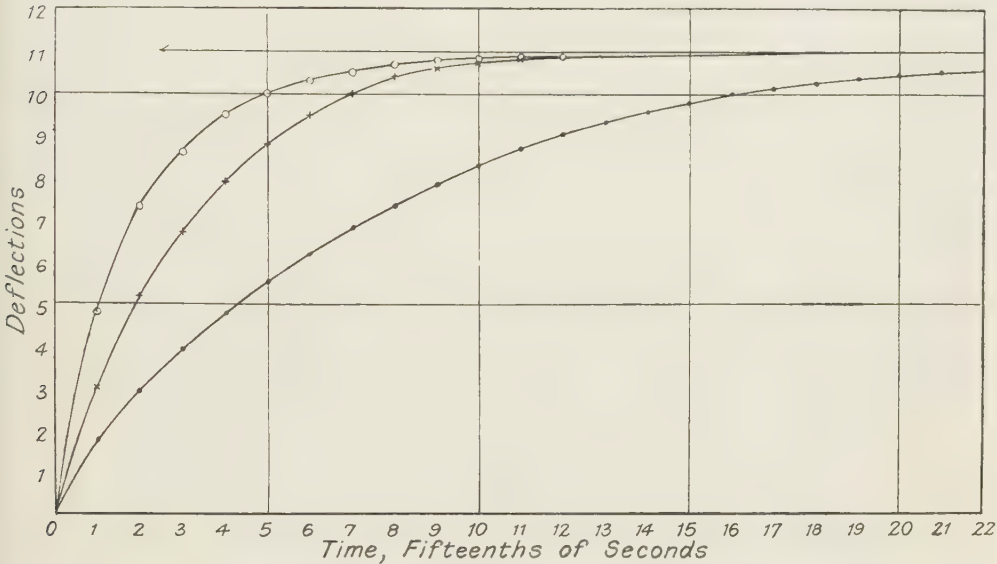

FIG. 24.—COMPARISON, UNDER SAME CONDITIONS, OF BOLOMETERS' RESPONSE.

ances of the three instruments, however, it is useful to compare them under conditions such that each will give identical final deflections. If these curves can be represented by the formula quoted, then we may shift the origins of the two curves of greatest amplitude, so that they shall all represent performances with the same final deflections. The new axes required for curves F and G are shown at Fa', Fb', Ga' and Gb', whilst the resulting comparative curves are shown together in Fig. 24. From an inspection of this it can be seen immediately what are the relative times for each bolometer to attain any given fraction of its full deflection. Taking the times for nine different deflections (2 to 10), the mean comparative speeds are :

$$\frac{F}{H} = 3 \cdot 90 \qquad\qquad \frac{G}{H} = 2 \cdot 21 \qquad\qquad \frac{F}{G} = 1 \cdot 77.$$

Roughly, therefore, the thinner film bolometer is four times, and the thicker one twice, as fast as the Lummer and Kurlbaum.

This determination of relative speeds depends on the accuracy with which the simple exponential formula represents experimental observations. It is found, however, that in all three cases substitution of corresponding values of t and θ in this expression give different values for the constant a. If the values of " a " so obtained are plotted in their turn against " t," it transpires that the variation of the constant in each case decreases smoothly with increasing time, following closely a logarithmic curve of the type

$$a = a_0 + K(t+c)^n$$

However, no formula of this type, representing the results with sufficient accuracy, suits our immediate purpose, and one falls back on representing this variation in the constant by means of the more empirical expression

$$a = b + ct + dt^2$$

Our original formula therefore becomes

$$\theta = \theta_\infty \{1 - e^{-(bt + ct^2 + dt^3)}\}$$

Choosing the range $t=0$ to 5, in order that the greater curvature may result in greater precision, this expression represents the results with sufficient accuracy, although, of course, extrapolation for values of t beyond 5 will be meaningless. The values of the constants obtained are

		b.	c.	d.
Film Bolometer F		$+0.765$	-0.107	$+0.0113$
Film Bolometer G		$+0.418$	-0.038	$+0.0045$
Lummer and Kurlbaum H		$+0.196$	-0.0245	$+0.00275$

The respective " speeds " will be given in each case by

$$\frac{d\theta}{dt} = \theta_\infty (b + 2ct + 3dt^2) e^{-(bt + ct^2 + dt^3)}$$

As a particular case, when $t=0$, the speeds will be

$$\left[\frac{d\theta}{dt}\right]_{t=0} = \theta_\infty . b,$$

and if the final deflections θ_∞ are taken, the same for each, to give a fair comparison the respective speeds work out as

$$\frac{F}{H} = 3.90 \qquad\qquad \frac{G}{H} = 2.13 \qquad\qquad \frac{F}{G} = 1.83$$

These figures refer only, of course, to the speeds of the respective " kicks " at the start of each bolometer's response. They will not, owing to the departure of the empirical formula from the simple exponential form, represent the merits of the three instruments at later stages. Further information is required as to what time each bolometer requires to attain some fraction of its full deflection. Examining this question, let the respective times be found for each to attain $1/n$th of its full deflection whatever θ_∞ may be.

The general equation concerned is

$$\theta = \theta_\infty \{1 - e^{-(bt + ct^2 + dt^3)}\}$$

or writing θ_D for $(\theta_\infty - \theta)$ and taking logs

$$\log_{10}\theta_D = -(bt + ct^2 + dt^3) \cdot \log_{10}e + \log_{10}\theta_\infty$$

and

$$\frac{\log\dfrac{\theta_\infty}{\theta_D}}{\log e} = bt + ct^2 + dt^3$$

Now if θ be put $= \dfrac{\theta_\infty}{n}$

then

$$\frac{\log\dfrac{n}{(n-1)}}{\log e} = bt + ct^2 + dt^3$$

or putting N equal to the constant expression on the left

$$N = bt + ct^2 + dt^3$$

For two instruments, therefore, F and H say, the respective times to attain $1/n$th of the final deflection θ_∞ in each case will be given by

$$b_F t_F + c_F t_F^2 + d_F t_F^3 = b_H t_H + c_H t_H^2 + d_H t_H^3$$

as both sides of the equation will equal N.

If, now, the expressions on each side of the equation be plotted against t, and any straight line drawn parallel to the axis of time to intersect the two curves, the values of t at the intersections will be inversely proportional to the respective speeds. A series of such straight lines can thus be drawn, and the mean value of the respective speeds obtained. The mean relative speeds are

$$\frac{F}{H} = 4 \cdot 25 \qquad\qquad \frac{G}{H} = 2 \cdot 39 \qquad\qquad \frac{F}{G} = 1 \cdot 78$$

Thus the actual mean speeds of the film bolometers relatively to the Lummer and Kurlbaum standard are slightly in excess of those obtained when $t=0$.

It is, however, clear that the graphical comparison shown in Fig. 24 is sufficiently close for the purpose of this Paper, where one is merely endeavouring to ascertain what advance has been obtained in speed. Various models of the same type would, of course, differ slightly amongst themselves in this matter of speed ; and it suffices to state that the thinner type is roughly four times, and the thicker twice, as fast as the Lummer and Kurlbaum.*

Thickness of Bolometer Films.

It has been seen that the thickness of the standard supporting collodion film was 0·00012 cm. As far as the sputtered metal film is concerned, interferometer measurements fail, the film being much thinner than a wavelength. One can only estimate the thickness from considerations of the specific resistance of the

---

* cf. Speed of sensitive thermopiles prepared by Dr. Moll. Recent Papers in Phil. Mag. and Proc. Phys. Soc.

metal and the superficial dimensions of the film. The thickness would be given for unit resistance by $\rho \times$ length $\div$ width. The latter are 0·75 and 0·25 in respectively, but the specific resistance is unknown. Patterson* has stated that the specific resistances of sputtered metals are several times greater than the metals in bulk. Can any estimation of the specific resistance of sputtered bismuth be made from the fact that the temperature coefficient of resistance is 0·00111, whereas that of the metal in bulk is 0·0042—roughly four times as great ? Supposing one accounts for the discrepancy on the supposition that only a portion of the total resistance is inherent in the metal itself, the remainder being imagined to exist as " bad contacts." In other words, within an aggregation of molecules the specific resistance of the metal applies, but between these aggregations the transference of electrons is much more difficult, requiring a greater potential gradient. If now the temperature be raised, the resistance due to passage within the molecule-aggregations will change, as it would in the metal in bulk ; whereas that due to the bad contacts would remain practically constant. Under these circumstances, if the temperature coefficient of resistance be only one-fourth of its true value, the resistance due to the metal itself will be one-fourth of the whole, provided the bad contacts are regarded as all in series with the molecule aggregations. The effective specific resistance of the film will therefore be four times that of the metal in bulk. If this view be correct, the thickness of a typical metal film works out roughly at 0·0000007 cm., or about 170 times as thin as the supporting collodion film.†

In that case the thickness of the metal film is negligible in comparison with that of the support, and the latter would be the vital factor in determining the speed. That there is something to be said for this view is the fact that the later type of collodion film, which is only one-half the standard thickness, gives, when sputtered, a bolometer which is twice as fast as the normal, although the thickness of the sputtered metal is the same in both cases.

It appears also that the thickness of the smoke blackening is negligible in comparison with that of the collodion film.

Film Thermo-piles.

Thermo-piles have been constructed on the same principle as the film bolometer described. In the first instance a single thermo-junction was used. The method of construction was exactly that used in the case of the bolometers, with the exception that one-half of the sputtered metallic strip would be of one metal, whilst the other half would be of another—a very slight overlap being allowed. Couples were made up in this way of the following pairs :—

Bi-Te	Pt-Au	Bi-Au	Bi-Ag

These worked quite satisfactorily, but the necessarily low E.M.F., combined with, as a rule, a high resistance rendered them of little use. It is interesting to note that the E.M.F.s observed were not usually those associated with the same metals in bulk. As an example, a Bi-Te couple gave 1 200 microvolts, whilst under the same temperature difference Pt-Au gave 126 microvolts, a ratio of roughly ten, whereas in bulk the ratio would be very considerably greater. Again, the order

---

* Phil. Mag., 6, 4 (1902).

† cf. Extremely thin translucent metal films prepared by C. Müller. *Engineering*, p. 199 (Feb. 12, 1926).

of sputtering is important. Tellurium must be sputtered before bismuth ; if the order be reversed, the deposit of the second metal is greatly retarded, or rendered abortive. The thermo-electric order should therefore be followed.

Attempts were made to construct instruments of ten or more couples. The procedure was to sputter one metal through a ladder-like mask, the apertures of which were of the same thickness as the rungs. The ladder would then be shifted half a step, so that the rungs would cover the sputtered portions and leave the interstices between open to sputtering by the second metal. Using bismuth and silver as the two metals, on account of their high thermo-E.M.F., low resistance and facility of sputtering, the method broke down owing to the apparent impossibility of sputtering bismuth through the tiny openings. The silver presented no difficulty, a though it appears that all metals are retarded when sputtered through small apertures. The experiments were not proceeded with, as those relating to bolometers appeared much more promising. In any case, owing to their high resistance, it would appear that a thermo-pile of this type, if made, would have to be used in such a way as to take advantage of the bolometric effect at the same time.

Acknowledgment.

In conclusion, I must express my gratitude to Prof. Callendar for his invaluable surveillance throughout the research.

Mr. Colebrook has taken a constructive interest in the design of apparatus and greatly facilitated their completion, the apparatus being made with admirable precision by Mr. Hellary. To Mr. Bradfield I am indebted for his excellent photographs of the drawings.

<div align="center">DISCUSSION.</div>

Dr. A. B. WOOD said that, knowing by experience the difficulty of such work, he would like to congratulate the author on having produced such thin and tenacious films. In describing Fig. 14 of the Paper, the author had stated that during the sputtering process the bismuth film passes repeatedly through a cycle in which its conductance increases up to a point and then suddenly ceases. Might not this be due to oxidation of the bismuth under sputtering conditions ? The greater part of the thickness of the author's films was contributed by the collodion. It might be of interest to note that very thin purely metallic films had been described by Carl Müller in a report of the Physikalische Reichsanstalt (February, 1926). These had been produced by the electro-deposition on copper of gold, silver, platinum, nickel or iron, the copper being subsequently dissolved away with the exception of a supporting ring. In this way gold membranes 0.02μ thick and nickel membranes 0.04μ thick and 6 cm. in diameter had been obtained. The speaker had produced, by rolling, metal films whose bolometer-effect reached half its final value in 1/10 sec.

Dr. EZER GRIFFITHS : I should like to congratulate the author on having worked out a difficult piece of technique. I think the bolometer might have applications in the study of radiation from gaseous explosions, etc. I should like further information on two points. (1) Whether the sputtered film is permanent in its physical properties. My experience with the sputtered films on the quartz suspension of an electrometer has not been encouraging. Perhaps this is an exceptionally difficult case as it is necessary to effect electrical contact between the film on an exceedingly thin quartz fibre and the hooks. (2) Whether the bolometer which the author employed as a standard of comparison was one which had the shortest period attainable with that form of construction.

Prof. F. L. HOPWOOD said that the Paper constituted a valuable guide to the technique of thin film production. Were the author's films permanent, or would their volatile constituents evaporate in a high vacuum ? He had seen another method successfully applied by Dr. A. Dauvillier in the case of magnesium, which was deposited on a collodion film by evaporation.

As regards the sputtering of aluminium, he had seen this carried out at the Cavendish Laboratory before the war by using an atmosphere of an appropriate gas, probably chlorine, whereas the Paper stated that aluminium could not be sputtered.

The AUTHOR, in reply to the discussion, said that the resistance of the films, when these had been aged, might be regarded as permanent, since it increases exponentially to a limiting value within a short time after manufacture. As regards the possible volatilization of the collodion in a vacuum, this certainly did not occur in the course of a week. Aluminium could admittedly be sputtered under appropriate conditions, but these were not the conditions necessitated by the present work.

V.—A HYGROMETER EMPLOYING GLYCERINE.

By Ezer Griffiths, *D.Sc., F.R.S.*, and J. H. Awbery, *B.A., B.Sc.*

(From the National Physical Laboratory.)

ABSTRACT.

The variation of refractive index of glycerine solutions in equilibrium with air of various humidities has been studied ; the time for equilibrium to be reached, when thin films of glycerine are used, has also been investigated.

It is concluded that this property may be used very conveniently in a hygrometer.

INTRODUCTION.

IN those hygrometers which utilise the change in some property of a hygroscopic body as a measure of humidity, there is frequently not only considerable time lag, but the indications depend to some extent on the past history of the material. Evidently this difficulty would be much lessened, if not eliminated, by using a liquid rather than a solid, such as hair or goldbeater's skin. Among hygroscopic liquids, glycerine is one of the commonest and most reproducible, and suggests itself for this purpose.

This idea had previously occurred to Giraud, who in 1913 published a brief Paper on the subject in the " Journal de Physique."

He employed cigarette paper soaked in glycerine, which he laid on the face of the prism of an Abbé refractometer, and determined the variation of refractive index with humidity. No details of his experiments are given beyond the remark that he employed a wet and dry bulb hygrometer as the standard for the humidity measurements.

We have repeated the experiments of Giraud, determining the relation between refractive index and humidity, but as a practical method of hygrometry found it to be somewhat unsatisfactory ; it was difficult to define the exact line of demarcation between the bright and dark portions of the field, an effect due to the diffusing effect of the cigarette paper. Trial showed that this could, in fact, be dispensed with, and the glycerine film applied direct to the glass prism. Fig. 1 gives a diagram of the apparatus, including the optical system.

A careful series of experiments was then made to ascertain the relation between the relative humidity of the surrounding atmosphere and the refractive index of a thin film of glycerine in equilibrium with it. Experiments were also made to find the time taken by a fresh film of glycerine to attain equilibrium with the atmosphere.

CALIBRATION.

To calibrate the instrument and obtain a curve of refractive index against humidity, it is necessary to expose the glycerine film to an atmosphere of which the humidity is known and is under control, whilst when equilibrium has been attained the refractive index must be read, which requires the manipulation of the refractometer.

This difficulty was overcome by the arrangement of apparatus shown in Fig. 2.
A vessel with a glass front was provided with means for altering the humidity of
the air in it, and with a dew-point tube and thermometer.*   In addition, a short length
of large diameter brass tube was inserted through one side, and a rubber glove
securely attached to this tube.

To carry out an experiment the refractometer with glycerine on the prism,
freely exposed, was inserted in the case, and the front closed.   The humidity being
adjusted to the desired value, a sufficient time was allowed to elapse for the establish-
ment of equilibrium, and then, by means of the rubber glove, the hand could be
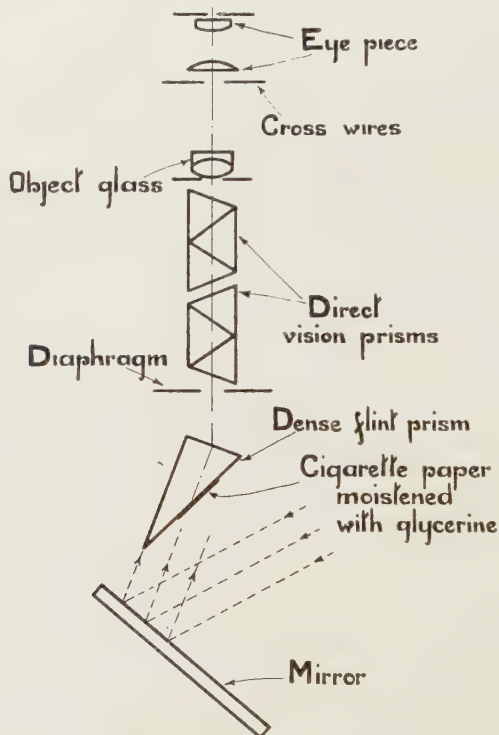

FIG. 1.

inserted in the case without opening it or otherwise disturbing the humidity, and
the cover provided on the Abbé refractometer closed, thus preventing the access of
air to the glycerine.   The method will be understood easily by a reference to Fig. 2.
The front of the case could now be opened, and the instrument withdrawn, and a
reading taken.

In this manner the calibration curve shown in Fig. 3 was obtained.   It may be
stated here that the results were the same, whether the glycerine was applied directly
or whether it was applied to the prism by means of cigarette paper.

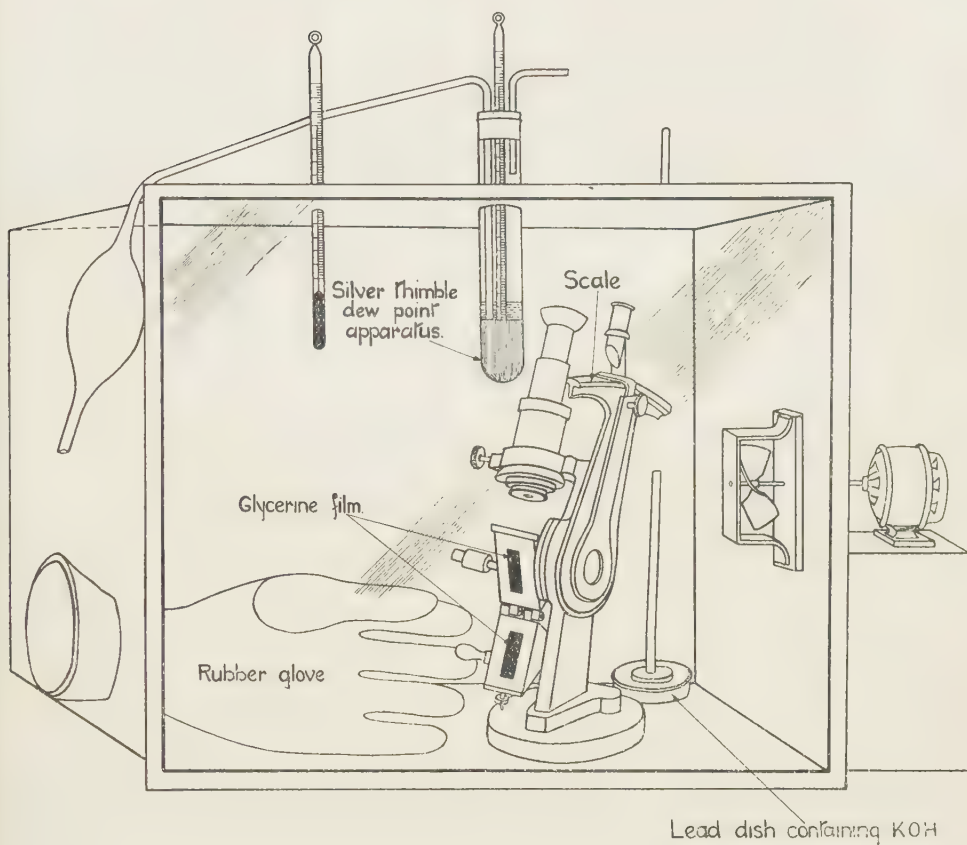* This vessel has already been described by one of us.   (*See* Proc. Phys. Soc., 1922).

Silver Thimble
dew point
apparatus.

Scale

Glycerine film.

Rubber glove

Lead dish containing KOH

FIG. 2.

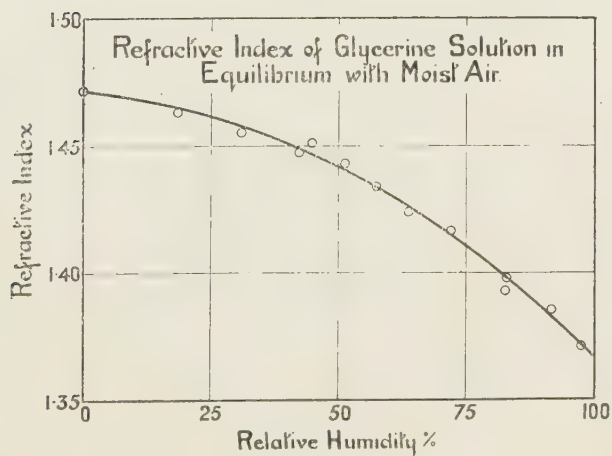Refractive Index of Glycerine Solution in
Equilibrium with Moist Air.

FIG. 3:

G

TEMPERATURE COEFFICIENT.

To investigate the temperature coefficient, a complete calibration was carried out in the same manner in a room of which the temperature was maintained at approximately 30°C. It was noticed that at this temperature, and at high humidities, where the glycerine solution is weak, the viscosity was so low that the liquid was inclined to run off the prism and readings were a little difficult. Nevertheless, the curve (Fig. 4) shows the effect of temperature very clearly. For comparison,
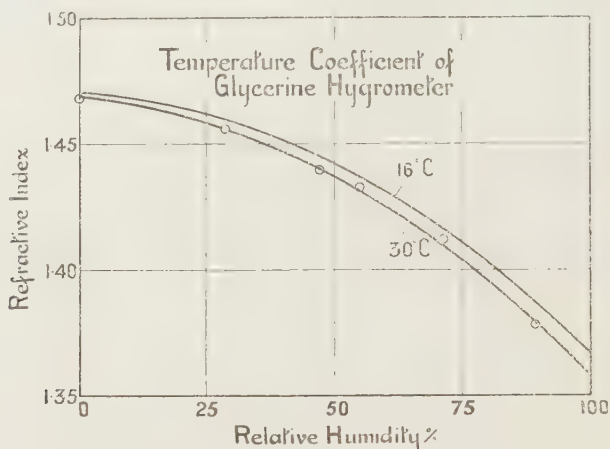

FIG. 4.

the smooth curve of Fig. 3 is there reproduced. An attempt was also made to obtain a calibration curve in a cold-storage chamber at −5°C. Unfortunately, the results were extremely erratic and no curve could be drawn through them. It is probable that freezing of the solution sometimes occurred at those concentrations for which the freezing point was above the temperature of the chamber.

Relative Humidity.	Refractive Index.	
	At 16°C.	At 30°C.
25	1·462	1·460
30	1·459	1·456
35	1·455	1·452
40	1·451	1·448
45	1·447	1·443
50	1·442	1·438
55	1·437	1·432
60	1·431	1·426
65	1·425	1·420
70	1·418	1·412
75	1·410	1·404
80	1·4〔2	1·396
85	1·394	1·387
90	1·385	1·378
95	1·376	1·369

TIME LAG OF THE INSTRUMENT.

To obtain data as to the time taken to reach equilibrium, the refractometer was placed in the calibration chamber referred to above, and allowed to become steady at a humidity of about 12 per cent. It was then transferred rapidly to the open room, where the humidity was 54, and readings taken at intervals. The curve is shown in Fig. 5, and it will be observed that half the change is completed in about 1·4 minutes ; however, the curve is not accurately exponential, and the time to cover 99 per cent. of the range is of the order of 15 minutes.

A second experiment was also made in which the instrument was transferred from a higher to a lower humidity in the same way, and the results for this are also shown in the same figure.

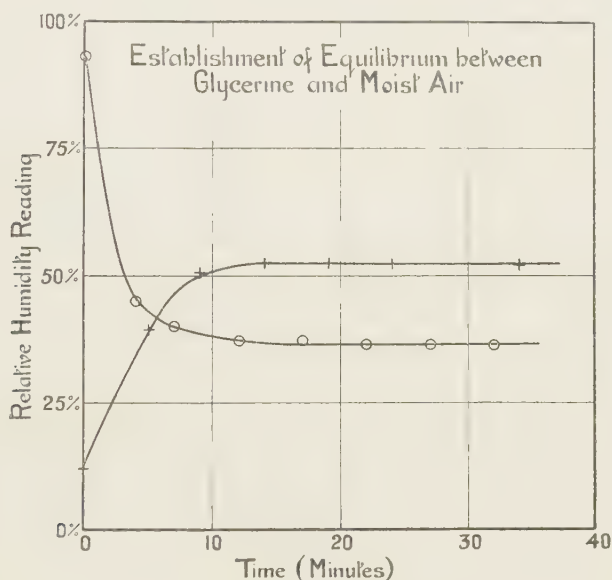It will be noted that the time lag is about the same in the two cases, but it must

FIG. 5.

be anticipated that the lag would vary with the exact thickness of glycerine actually placed on the prism surface.

It may be of interest to calculate approximately the concentrations of gly-cerine concerned at the usual humidities. For this purpose two methods are avail-able. The refractive indices of glycerine solutions for the *D* lines have been measured by Strohmer at 17·5°C. from concentrations of 50 to 100 gms. per 100 gms. of solu-tion ; his curve could be extrapolated with some certainty, since the refractive index of water gives the end-point of the curve. Unfortunately, our calibration is for white light and his for sodium, but the difference is comparatively small, and no correction was applied. The concentrations for the refractive indices corresponding to humidities of 10, 20, 30 per cent. etc., were read off from this curve, and are shown in the table below.

A second method of estimating the concentrations makes use of the humidities directly, utilising the vapour pressure measurements of Dieterici (at 0°C.) for concen-trations from 20 to 400 gms. glycerine per 100 gms. of water. This again is not

directly comparable with our experiments, owing to the temperature, but, assuming his value for the vapour pressure of water at 0°C., the vapour pressures at other humidities were calculated and the corresponding concentrations read off.

Converting both sets of results to the same units, we obtain the following results :

Relative Humidity. %	Concentration (% by weight of glycerine).	
	From refractive index.	From vapour pressure.
0	100	100
10	98	...
20	94	...
30	90	...
40	85	85
50	80	79
60	73	71
70	66	62
80	58	51
90	48	33
100	32	0

The agreement is good, considering the nature of the data, up to 80 per cent. humidity. Above that, it is clear that there must be discrepancies, since by the nature of the instrument there is always glycerine present, even at the highest humidities. Thus, even at saturation, the refractive index does not fall off to the value for pure water, whereas the curve of concentration against refractive index does do so.

PRACTICAL CONSIDERATIONS.

The advantages and disadvantages of the instrument may be briefly summarised as follows :—

(1) Although it requires a definite setting to be made before the humidity can be obtained, the refractive index scale could be engraved directly in humidities, so that the instrument is simpler than a wet-and-dry bulb hygrometer, or than the dew-point instrument, in that there are no calculations necessary.

(2) Its lag is about 15 minutes. In many cases this would not be excessive.

(3) It is portable and reasonably robust.

ACKNOWLEDGMENT.

DISCUSSION.

Prof. C. V. Boys (communicated) : I have read Dr. Griffiths's Paper on a glycerine hygrometer with especial interest, as I have long intended to try a glycerine hygrometer consisting of a piece of paper wetted with glycerine and suspended from one arm of a special light balance most easily made with wheat-straw, needles and sealing wax, so as to indicate perhaps 10,000ths of a grain, but with sufficient stability to remain within its arc of swing for such variations of relative humidity as, e.g., 50 per cent. to 80 per cent. or 90 per cent. With such stability the delicacy of weighing might be less but still ample. Such a hygrometer could be made to go in a space not more than 2 in. long and 2 in. high, and a lag for half an hour or so would for many purposes be quite immaterial.

Each instrument would, I fear, need to be calibrated separately, but the information supplied by Dr. Griffiths indicates that it might well give consistent results, and that the time of arrival would not be excessive.

VI. –EFFECT OF WORKING ON THE PHYSICAL PROPERTIES OF TUNGSTEN.

By J. W. Avery, *B.Sc., D.I.C.*, and C. J. Smithells, *D.Sc.*

(Communication from the Staff of the Research Laboratories of the General Electric Company, Ltd., Wembley.)

Abstract.

Changes in the density and resistivity of tungsten during swaging and drawing have been investigated.

The densities of pure and thoriated tungsten (0·63 per cent. thoria) from the sintered bar down to wires 0·02 mms. in diameter are given. The experimental advantages of the use of benzene as the displaced liquid are mentioned.

Measurements of the densities of specimens cleaned in successive stages by etching reveal the presence of low density surface layers.

Variations of heat treatment likely to occur in practice are shown to have no appreciable effect upon the density of worked tungsten.

The density rises rapidly during swaging to a maximum value within 0·5 per cent. of the density of the perfect tungsten crystal. Further working produces a steady fall in density, which becomes more marked in the finest sizes.

Measurements have been made of the resistivity of the same specimens.

The resistivity falls rapidly in the early stages of working and reaches a minimum when the density is a maximum. It then increases at a uniform rate, which is approximately an exponential function of the diameter

I. Density and Resistivity.

THE structure developed in a drawn tungsten wire when heated above its recrystallisation temperature depends upon the mechanical treatment to which the metal has previously been subjected. In particular, it has been found that the percentage reduction in cross-sectional area and the temperature at which the metal has been worked have a marked influence on the structure of the recrystallised wire. The changes which take place in the physical properties of the wire during working have been measured in order to throw light on the mechanism of recrystallisation. In the present Paper the results of measurements of density and resistivity are given.

Part I.—Density.

The density of the perfect tungsten crystal can be calculated from the lattice spacing as determined by X-ray measurements and the atomic weight. The most accurate determination is that of Davey,* who found a value of 3·155±0·001Å. for the lattice constant, using a sample containing 99·9995 per cent. tungsten. Taking the atomic weight as 184·0, this gives a value for the density of 19·32±0·02 qms./cm³.

The changes in density which take place during the swaging and drawing of tungsten rods have been investigated by a number of workers, but their results do not show satisfactory agreement. The values found by Lorentz (Table I) show a progressive fall in density with decreasing diameter, whilst Schriever† found an increase in density (Table II), the value for the finest wires being considerably

---

* Davey, Phys. Rev., 25, 753 (1925).

† Schriever, Iowa Acad. of Science, 24, 235 (1917).

higher than that calculated from X-ray measurements. The density does not, however, appear to change in a regular manner.

TABLE I.—*Density of Worked Tungsten (Lorentz).*

Material.				Diameter (mms.).	Density.
Swaged rod	...	...	...	1·27	19·1
Drawn wire	...	...	...	0·51	18·8
,,	,,	...	...	0·254	18·5
,,	,,	...	...	0·127	17·9

TABLE II.—*Density of Worked Tungsten (Schriever).*

Material.				Diameter (mms.).	Density.
Drawn wire	...	...	...	0·227	19·13
,,	,,	...	...	0·176	19·03
,,	,,	...	...	0·126	19·48
,,	,,	...	...	0·078	19·35
,,	,,	...	...	0·024	20·26

Geiss and Van Liempt* have measured the density over a wide range of wire sizes, and their results, given in Table III, show a steady increase in density down to the finest sizes, for which the values closely approach the theoretical value of 19·32.

TABLE III.—*Density of Worked Tungsten (Geiss and V. Liempt).*

Material.				Diameter (mms.).	Density.
Sintered ...	...	...	...	...	10—12
Formed ...	...	...	...	15·0	16·88
Hammered	...	...	...	14·8	17·62
,,	...	...	...	11·8	18·28
,,	...	...	...	6·2	19·16
,,	...	...	...	5·0	19·19
,,	...	...	...	3·85	19·22
Drawn	...	...	...	0·150	19·23
,,	...	...	...	0·110	19·22
,,	...	...	...	0·020	19·41±0·04
,,	...	...	...	0·0125	19·28±0·06

In view of the fundamental differences in the results quoted, the authors have repeated the measurements both for pure tungsten and for tungsten containing 0·63 per cent. thoria, and have studied the effect of some variations in the mechanical and thermal treatment of the wires.

Materials.

Tungsten rods 5·6 × 5·6 × 17·5 mms. were prepared from metal powder, which was pressed and formed in the usual manner, of which numerous accounts have been published.†

The following particulars give the essential difference between the two batches of metal used in the investigation.

Metal A.—Pure Tungsten.

The sintered bars contained more than 99·99 per cent. tungsten, and had a fine grained structure.

---

* Geiss and Van Liempt, Annalen der Physik., 77, 105 (1925).
† Dudding and Smithells, B.E.A.M.A , 13, 221 (1923).

Metal B.—Thoriated Tungsten.

The sintered bars contained 0·63 per cent. ThO_2, other impurities being less than 0·01 per cent. The bars had a very coarse structure.

MECHANICAL WORK.

After forming at about 3100°C., the bars were sufficiently strong to be worked mechanically. The preliminary reduction was carried out in swaging machines in which the bar was hammered to a round section and increased in length. The temperature, which was lowered progressively, as shown in Table IV, was throughout below the temperature at which any visible recrystallisation takes place in the metal.

TABLE IV.

Wire Diameter. Mms.	Swaging Temperature. Degrees C.
6·0	1,300
4·0	1,200
3·0	1,100
1·5	1,000
1·0	900
0·8	750

After the metal had been reduced to a diameter of 0·8 mm., further reduction was carried out by drawing through diamond dies. The reduction in diameter at each step was between 8 and 10 per cent. The wire was heated before entering the die by passing an electric current through the wire, the temperature being lowered progressively from 800° to 500°C. as the wire diameter decreased.

METHOD OF MEASUREMENT.

The density of wires larger than 1 mm. in diameter may be determined by weighing in air, and in distilled water, using a sensitive chemical balance, the samples weighing from 10 to 50 grams.

Considerable difficulty was found in obtaining an equal accuracy with finer wires. A torsion balance, which would have enabled rapid readings to be taken, was not found to give sufficient accuracy, and eventually a chemical balance weighing to $\pm0·0001$ gm. was used. It was hoped to obtain increased accuracy by using as the displaced liquid, methylene iodide, which has a density of 3·34; but surface tension effects, where the supporting wire passed through the surface, more than counterbalanced the advantages of increased upthrust. Water was found to be as bad in this respect, even when a fine and well-cleaned platinum wire suspension was used. It was not the magnitude of the surface tension which caused trouble, but its irregularity of action, by which it seemed to cling to the wire cutting the surface, and to hold it even against several milligrammes excess weight on the opposite side of the balance.

Alcohol and benzene were both found to give freedom from this source of difficulty and error, the suspension wire passing smoothly through the surface and the balance being as sensitive to added weights as if the body were being weighed in air.

In order to obtain a sufficiently accurate value of the density of the finer wires a considerable length of wire had to be used. This necessitated winding it in a loose

coil. It was found extremely difficult to free such a coil from air bubbles when immersed in water, even by boiling under reduced pressure. Distilled water also has an appreciable oxidising action on fine tungsten wires. The use of benzene avoids both these difficulties. By boiling the coil of wire for a few seconds in benzene in the vessel in which it is to be weighed all sign of air bubbles is removed ; and the benzene has no chemical action on the tungsten, and cools conveniently rapidly.

Benzene was therefore used in conjunction with a sensitive chemical balance to determine the density of the finer wires.

The benzene was re-distilled from " pure recrystallised " benzene, and a constant boiling fraction taken. Its density was determined by the displacement method, using two hollow glass " sinkers " ballasted with lead, which were weighed in the benzene and in distilled water. After correcting for the expansion of the glass sinkers, this gave the density as 0·8873 at 12°C. in air. The accepted relation* between density and temperature for benzene was used in the subsequent work. The fine wires were wound into coils on a former of such design that the coils could be secured and removed from it intact. This former consisted of a hollow steel cylinder divided into three parts by three parallel axial cuts, fitted on to a steel core. The whole was held together by two brass clips, with nuts and bolts to tighten them. Three to five short pieces of thin tungsten wire were held in place by and between the clips, and the wire under test was wound on top of them. The ends of the short pieces were then pulled out of the loosened clips, and twisted together, as also were the two ends of the coil. On removal of the steel core, one of the three sections of the outer split cylinder was pushed out of place and the coil easily removed intact. Tightening the binding-wires then gave a coil of fine wire about one inch in diameter, which was convenient to handle for density measurements.

This coil was boiled for a few seconds in a separate lot of benzene before being boiled in the benzene in which it was finally weighed.

The finer wires were suspended by a tungsten wire 0·05 mm. in diameter, and the larger ones by a nickel wire 0·13 mm. diameter. Correction for the weight of the suspension wire, and the surface tension effects upon it, was made by weighing it alone partly immersed in the liquid as when in use.

After being weighed suspended in benzene, the coil was dried by heating on a watch-glass over a steam bath, allowed to cool and re-weighed.

Experimental Results.

Tungsten wire must be lubricated with graphite during drawing, and the finished wire has a shiny black surface. Chemical analysis of several samples of wire 0·05 mms. in diameter showed that the weight of carbon on the wire was 0·05 per cent. of the weight of the wire. This corresponds to a layer 0·05μ thick, which in the case of wire 0·05 mm. in diameter would only affect the density by 0·35 per cent. The first measurements were, therefore, made on the wires as drawn, and without any preliminary cleaning beyond boiling in benzene.

The results of these measurements for Metals A and B are summarised in Table V and shown graphically in Fig. 1.

---

* Landolt Börnstein, Tabellen, 1025 (1912).

The accuracy of the determination varies according to the weight of material available for each specimen, and this has been indicated in the table.

TABLE V. —*Density of Tungsten Wires as Drawn (Black Wire).*

Material.		Diameter. Mms.	Density.*			
			Bar No.	Pure Metal A.	Bar No.	Thoriated Metal B.
Formed bar	...	(6.02) – (6.24)	107	17·29	35	17·33
,, ...	...	,, ,,	...	...	67	17·21
Swaged rod	...	5·1	112	18·34	31	18·41
,, ...	...	4·0	...	...	30	18·94
,, ...	...	2·95	102	19·10	32	19·08
,, ...	...	2·03	104	19·10	33	19·07
,, ...	...	1·4	111	$19·1_2$	37	$19·0_4$
,, ...	...	1·05	111	$19·0_9$	76	$19·0_0$
Drawn wire	...	0·61	102	19·00	37	...
,, ...	...	0·50	...	...	33	$18·8_5$
,, ...	...	0·295	110	19·05	37	$18·8_1$
,, ...	...	0·150	108	$19·0_0$	33	18·79
,, ...	...	0·140	...	...	37	18·75
,, ...	...	0·117	...	...	33	$18·7_1$
,, ...	...	0·093	...	...	37	$18·7_1$
,, ...	...	0·072	108	$18·8_0$	33	$18·6_2$
,, ...	...	0·058	...	...	37	18·7
,, ...	...	0·047	108	$18·7_5$	33	18·4
,, ...	...	0·030	...	...	37	18·4
,, ...	...	0·030	...	...	33	18·3
,, ...	...	0·021	...	...	33	18·2±0·2
,, ...	...	0·021	...	...	37	17·8 ±0·2

The general shape of the density-diameter curve is the same for both metals. A rapid increase in density occurs in the early stages, when the porous bar is compacted by hammering, and after reaching a maximum a steady fall in density occurs,
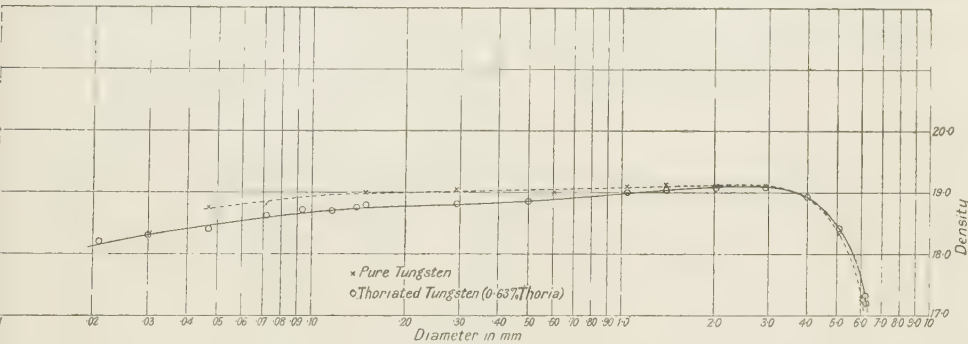

FIG. 1.—DENSITY OF PURE TUNGSTEN AND THORIATED TUNGSTEN WIRE (UNCLEANED).

which in the case of the thoriated metal (Metal B) becomes very marked in the finest sizes. Below 0·03 mm. diameter these wires became difficult to draw, and the very low values may be attributed to internal splits.

Taking the density of the thoria particles as 10·0, the theoretical maximum

* The accuracy is indicated by the significant figure.

density for Metal B is 19·22, whilst that for pure tungsten is 19·32.   It is, therefore, clear that neither metal attained its full theoretical density.   It seemed possible that this, and also the subsequent fall in density, might be due to foreign material on the wire surface, since this would produce a greater effect on the smaller wires. The effect of removing the surface layers from the specimens was therefore investigated.

EFFECT OF CLEANING.

A " black " tungsten wire can readily be cleaned by raising it to incandescence in dry hydrogen.   To determine the total weight of volatile material removed in this way, about 60 metres of fine wire of Metal A (diameter 0·045 mm.), cut into short lengths, were flashed in hydrogen.   The total loss in weight represented 0·51 per cent. of the weight of the wire.

Repeating the operation with the same wire produced no further change in weight, showing that the original loss was not due to oxidation.   Since the carbon represents only 0·05 per cent. by weight, the bulk of the volatile material most probably consists of oxides of tungsten.   Tungsten is readily oxidised at the temperature at which it is swaged, and a certain amount of oxidation occurs before the graphite lubricant, which protects the finer wires, is used.

The black wire can be cleaned by treatment with reagents which dissolve tungsten oxides, and so loosen the graphite.   Hydrogen peroxide and ammonia, which reacts slowly, was found to give easy control ; but for more vigorous etching a hot solution of sodium peroxide, following by boiling in ammonia, was used.   The specimens of Metal A previously used were thoroughly cleaned in this way, and their densities re-determined.   The densities of the cleaned wires were found to be higher than before, the effect being most marked with the finer wires.   The results are given in Table VI and Fig. 2, where the values for the uncleaned wires are reproduced for comparison.   The maximum density, which is now only 0·5 per cent. below the theoretical value, still occurs at the same diameter, but the fall in density on further working is much less marked.

Similar determinations were made on a few samples of Metal B, and the results, which show changes of the same order, are included in Table VI.

TABLE VI.—*Comparison of Densities of Black and Cleaned Wires.*

Material.					Diameter. Mms.	Density.	
						Black.	Cleaned.
Metal A, formed	bar	...	...		(6·02)	17·29	17·29
,,	swaged	...	...	...	5·1	18·34	...
,,	,,	...	...	...	3·0	19·10	19·20
,,	,,	...	..	...	2·03	19·10	19·22
,,	,,	...	...	...	1·4	$19·1_2$	$19·2_4$
,,	,,	...	...	...	1·05	$19·0_9$	$19·2_1$
,,	drawn	...	...	...	0·61	19·00	...
,,	,,	...	...	...	0·295	19·05	19·21
,,	,,	...	...	...	0·150	$19·0_0$	$19·2_4$
,,	,,	...	...	...	0·072	$18·8_0$	...
,,	,,	...	...	...	0·048	$18·7_5$	$19·1_9$
,,	,,	...	...	...	0·036	...	$19·0_7$
Metal B, swaged		...	...	...	4·7	18·82	18·86
,,	,,	...	...	...	2·03	18·95	19·08
,,	drawn	...	...	...	0·048	18·54	18·92

These large effects indicate that a comparatively thick layer of low density material exists on the surface of the wire as drawn, and an attempt was made to determine its nature.

It was hoped that by etching off successive small layers from the surface, and determining the change in density, some information about the thickness and density of the surface material might be obtained. This, however, involved an accuracy of about 0·1 per cent., which was found extremely difficult to obtain. The chief errors arose from temperature variations in the benzene due to evaporation, and adsorption of moisture on the wire surface. To obtain sufficiently accurate weighings with wire 0·05 mm. in diameter a coil of 800 metres was necessary, and this has a surface of over 1,000 sq. cms.

A number of determinations were finally made, which, whilst not obtaining such a high accuracy, indicate the nature of the surface layers. These results are summarised in Table VII.

TABLE VII.—*Effect of Progressive Cleaning on the Density of Tungsten Wire.*

Wire.	Diameter. Mms.	Percentage weight removed by etching (Total).	Density of remaining wire.	Average depth (below original surface) of each layer removed. Mms.	(Mean) Density of each layer removed.
*Thoriated	2·03	0	18·94$_5$		
				0·0030	10
		0·60	19·06		
				0·0090	17
		1·65	19·08$_5$		
				0·0132	20
		2·16	19·08		
Metal A ... Pure Tungsten	1·4	0·00	19·12$_3$		
				0·0016	8·0
		0·38	19·22$_3$		
				0·0041	11·5
		0·86	19·23$_4$		
				0·0060	13·5
		1·38	19·23$_8$		
Metal B ... (Thoriated)	0·048	0·00	18·5$_4$		
				0·00023	10·0
		1·8$_6$	18·80		
				0·00055	15·0
		3·8$_7$	18·92		
				0·00101	19·5
		9·3$_1$	18·89		
				0·00164	19·0
		14·5	18·91		

Whilst the accuracy obtained is not high, these results show that the outer layers of the wire as drawn have a low density, which increases until the density of the tungsten composing the main part of the wire is reached.

In the case of wire 0·048 mm. in diameter these low density layers are sufficient to reduce the mean density by 2 per cent.

* This was not of the same batch of metal as B.

In each case the first layer removed evidently contained material, probably oxides of tungsten, of a much higher density than graphite. Still higher densities of 12 and 15, too high for tungsten oxides, suggest the presence of some " loose " tungsten mixed up with the material.

Effect of Heat Treatment.

Considerable modifications in the normal methods of working tungsten are possible, which might account for the differences in density found by different observers. The effect of recrystallising during working was investigated in the case of Metal B. A number of bars were swaged to a diameter of 5·1 mms., and then heated to 3,000°C. in dry hydrogen by the passage of an electric current. It was found that a period of two minutes was sufficient to cause complete recrystallisation. The bars were then worked into wire in the usual way, and the density determined at various stages in drawing. The measurements were made on the wires as drawn,
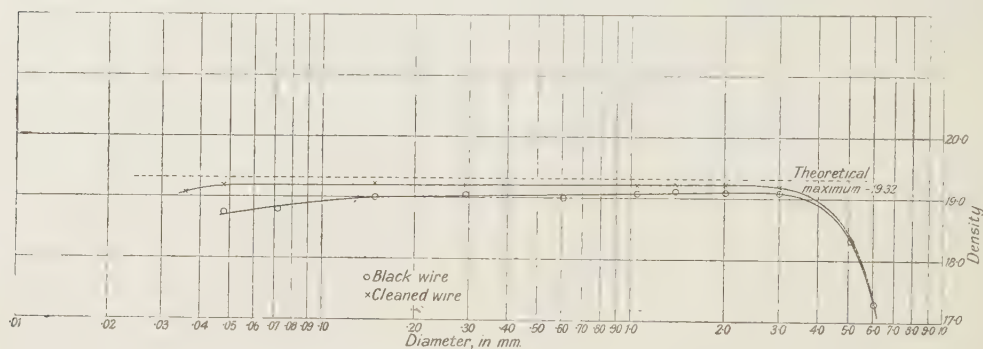

Fig. 2.—Density of Drawn Tungsten Wire before and after cleaning

and the results included in Fig. 1. These points lie on the normal curve, and show that no appreciable effect on the density is produced by the recrystallisation.

The effect of variations in the method of heating the wire before it enters the die was investigated for the same metal. Two rods were drawn to a diameter of 0·150 mm. in the usual way ; but for the subsequent dies one was heated by the passage of an electric current, and the other by means of a gas burner. Although the maximum temperature was the same in both cases, this could be maintained over a much larger length with gas heating, which is equivalent to heating the wire for a longer time before it enters the die.

Density measurements on both wires showed differences which were within the limits of accuracy of the determinations, and indicate that the general shape of the density curve is unaffected by these changes in heat treatment.

Discussion of Results.

It appears from these results that when pressed and sintered bars of pure tungsten are reduced by swaging the first effect is to compact the metal and eliminate the voids, the density rapidly reaching a maximum, about 0·5 per cent. less than the theoretical value. Further reduction in diameter by swaging and drawing

produces a slight drop in density over a long period, but this increases more rapidly when the diameter is below 0·05 mm.

Tungsten containing thoria behaves in a similar manner, the density throughout being lower on account of the lower density of the thoria. The fall in density as the wire becomes finer is, however, more marked with thoriated tungsten, particularly in the very fine sizes, where the wire is liable to split and break in drawing.

Variations in heat treatment during drawing, covering the extremes likely to occur in practice, produce no appreciable effect on the density of the drawn wire.

These results are not in agreement with those of Geiss and V. Liempt, who found a steady increase in density down to the finest sizes. It is possible that the methods used by them produced wires with different characteristics, although this seems less probable in view of the authors' inability to influence the density by wide variations in the method of drawing.

The fall in density appears to take place in two stages. The slight fall between 3·0 and 0·05 mms. suggests that the metal is deforming by slip on crystal planes, involving break up of the original crystals. The much more rapid decrease in density below 0·05 mm. diameter is undoubtedly due to the incipient formation of longitudinal splits, which eventually become visible under the microscope. Such splits are much more prevalent in thoriated wire, in which the fall in density is most marked.

Part II. —Resistivity.

The resistivity of tungsten wire in the annealed condition has been determined by Worthing,[*] who obtained the value $5·47 \times 10^{-6}$ ohm. cms. at 20°C. Tsukamoto[†] has measured the resistivity of swaged and drawn tungsten at various stages during the manufacture of fine wire. After an initial fall corresponding to the increase in density which takes place during the first swaging processes, he found an increase in resistivity which was approximately an exponential function of the diameter. The authors have measured the resistivity of the specimens of Metal B used in the density determinations described in Part I of this Paper.

Method of Measurement.

The method adopted was to measure the potential difference between two points on the specimen, and between the terminals of a standard resistance in series with the specimen and carrying the same current. A Crompton instrument arranged as a millivolt potentiometer was used.

The finer wires were stretched lightly between two terminals on a wooden base and across two razor edges, which acted as potential leads and also defined the length of the specimen. The ends of the thicker rods were soldered to brass terminals, which were connected to the current leads. Fine nickel wires 0·1 mm. in diameter were spot-welded to the specimen near either end as potential leads, the distance between them being accurately determined with a cathetometer.

The temperature was measured with a thermometer placed close to the specimen. The currents used were insufficient to produce any measurable change in the temperature, and no change in the potential difference-current ratio was found when

---

[*] Worthing, Phys. Rev., Vol. 18, p. 144 (1921).
[†] Tsukamoto, Nagaoka Anniversary Vol., p. 409 (1925).

the current was increased 900 per cent. The determinations were made on the drawn wires without preliminary cleaning. The diameter was calculated from the weight of a measured length of wire, using the appropriate value of the density found in the earlier experiments.

Finally, the resistivity at 20°C. was calculated, using the value for the temperature coefficient found by Worthing—namely, 0.004×10^{-6} ohm. cms. per degree C. Actually the temperature only varied from 20°C. by one or two degrees during the measurements. The resistivity curve for cleaned wires would have a closely similar form, the values for the finest wires being only 3 per cent. less even if the surface layers were non-conducting. The results obtained with Metal B are given in Table VIII and shown graphically in Fig. 3.

TABLE   VIII.—*Resistivity of Worked Tungsten.*

Diameter (mms.).	Resistivity (20° C.) ohm. cms.
(6·24)	$6·13 \times 10^{-6}$
5·1	5·58
4·0	5·47
2·95	5·48
2·03	5·45
1·40	5·47
0·80	5·73
0·69	5·70
0·375	5·92
0·235	6·16
0·150	6·24
0·131	6·52
0·117	6·57
0·100	6·76
0·086	6·48
0·072	6·80
0·060	6·62
0·052	6·99
0·047	6·92

EXPERIMENTAL RESULTS.

As the ingot is worked the resistivity of the metal falls, and reaches a minimum value of 5.4×10^{-6} at a diameter of about 2·5 mms. Further working produces a steady increase in the resistivity, the value at 0·05 mm. being about 7.0×10^{-6}. When the resistivity is plotted against the logarithm of the diameter, as in Fig. 3, the curve is nearly a straight line over the range 1·0 to 0·05 mms.

The initial fall in resistivity follows the increase in density which takes place during the early steps of swaging, and the minimum resistivity occurs at the same point as the maximum density.

The subsequent increase in resistivity is much greater than can be accounted for by the slight fall in density in wires less than 1·0 mm. in diameter, and must be the direct result of the deformation which the metal has undergone. The points representing individual observations on the finer wires lie considerably off the best smooth curve, and greatly exceed the errors of measurement. These variations appear to have a real significance, and must be attributed to the method of working

the metal. There are a number of factors involved in drawing fine wires which might account for such variations of which the most important are probably :

Condition of the die.

Temperature of the wire.

Percentage reduction at each draught.

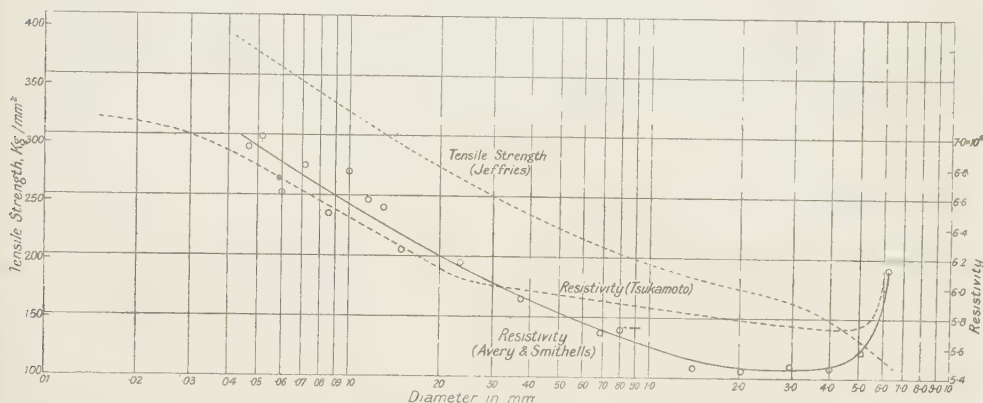Of these variables, the temperature of the wire can most easily be controlled.

FIG. 3.—RESISTIVITY AND TENSILE STRENGTH OF DRAWN TUNGSTEN WIRE (0·63% THORIA).

EFFECT OF DRAWING TEMPERATURE.

Specimens were available which had been drawn using gas and electric heating as already described. The densities showed no appreciable differences. The resistivities are given in Table IX.

TABLE IX.

Diameter (mm.).	Resistivity.	
	Electric Heating.	Gas Heating.
0·131	$6·34 \times 10^{-6}$	$6·13 \times 10^{-6}$
0·114	6·28	6·12
0·100	6·32	6·19
0·086	6·43	6·37
0·072	6·60	6·38
0·060	6·79	...
0·051	6·85	6·61
0·048	6·86	6·62

These results show that the electrically heated wires have a considerably higher resistivity than those which had a more prolonged annealing due to the gas heating. The difference is larger than the variations referred to in the previous section, and supports the view that they are due to such uncontrolled variations as might be expected in the wire drawing process.

Conclusions.

The general shape of the resistivity curve is similar to that found by Tsukamoto for wire containing 1 per cent. thoria.

The increase in resistivity when the metal has suffered a large reduction in cross section cannot be attributed to the change in density, but must be the result of changes in the structure of the metal. It is interesting to note that the curve connecting tensile strength and diameter is of the same shape as the resistivity curve for wires less than 2·0 mms. in diameter. Jeffries* values for the tensile strength of swaged and drawn tungsten wires are plotted in Fig. 3, and the comparison indicates that the changes in both tensile strength and resistivity depend upon the same structural changes in the metal.

DISCUSSION.

Dr. H. Borns : Mr. Avery has said that water adhered to some spots on the tungsten wires. Had these spots possibly been touched with the fingers ?

Dr. E. H. Rayner said that the drawing of tungsten is a very wonderful process, considering that a 6 in. bar of the metal is pulled out to a length of a mile or two by 50 or 100 successive drawings. At each drawing it is passed through a bath of graphite, and he would like to know what evidence had been found as to the extent to which graphite fails to penetrate into the substance of the metal. The claim that it remains almost entirely on the surface was a surprising one.

Sir Richard Paget enquired whether a relation had been traced between the resistivity and tensile strength of the wires ?

Dr. Smithells, in reply to the discussion, said that wires had been tested for carbon after drawing, by chemical analysis, by resistance measurements, by the spectroscope, and by heating to incandescence. It had been found extremely difficult to retain more than 0·3 per cent. of carbon in worked wire, even when carbon was deliberately added to the metal. Analysis of an ordinary wire showed about 0·05 per cent., and this was mainly in the surface layers. If carbon were present as carbide, the fact would at once be apparent from the effect of carbide on the resistivity and ductility of the metal. The tensile strength of the specimens had not been tested, but the upper curve in Fig. 3, which embodies the results obtained by Jeffries for the tensile strength of other specimens, was markedly parallel with the resistivity curves for small diameters. In reply to Dr. Borns' question, the wires were not touched by hand after cleaning. It was not the case that water adhered to some spots on the tungsten wire, but that it clung to certain points on the suspension wire even after every precaution had been taken to clean it.

* *See* Forsythe and Worthing, Astrophysical J., Vol. 61, p. 148 (1925).

DEMONSTRATION OF SELENIUM CELLS.

By Prof. Hans Thirring, Professor of Theoretical Physics in the University of Vienna.

THE sensitivity of a selenium cell depends a great deal upon the thinness of the selenium coating, since only the surface layer is influenced by the light. Experience has shown that with the condenser type of cells the thickness of the selenium coating can be reduced down to any desired value by the capillary action of suitably chosen electrodes. The condenser type is convenient also for making selenium cells of very small light-sensitive area, without unduly increasing the resistance. The following table indicates the approximate resistances of examples of the standard types of cells shown, which have been made according to the author's patents by Messrs. J. Malovich & Co., in Vienna.

Cell No.	Light-Sensitive Area.	Current in microamperes at 12 volts.	
		Dark.	Illuminated 100 metre candles.
195	Circular, 1 mm. diam....	0·2	2·5
753	Rectangular, 0·14 mm. × 10 mm.	0·1	3·8
925	Rectangular, 1 mm. × 10 mm.	0·1	6·0
1,301	Circular, 5 mm. diam....	3·0	24·0
1,312	Rectangular, 7 mm. × 35 mm.	72·0	432·0

The advantage of a small light sensitive surface lies in the fact that a focussing lens which concentrates the light on the cells can be used. Since the ratio between dark resistance and light resistance depends on the intensity of illumination (energy per unit area), a small cell can be used more efficiently than a large one with equal electrical properties.

It does not seem to be possible to remove all the deficiencies which are naturally inherent in selenium cells. Among these deficiencies the following may be mentioned :—

(a) The resistance is not a linear function of the intensity of illumination ;

(b) It has a temperature coefficient ;

(c) The reaction to light is not instantaneous.

Selenium cells should, therefore, be used in an arrangement which compensates as far as possible these deficiencies for the given purpose. A very efficient device is the use of the cells with an intermittent illumination of acoustical frequency, the cell being coupled with an amplifier. It is important in this case that there should be no spontaneous rapid fluctuations of the resistance, for these give rise to grating noises. In this respect also the cells shown are superior to those of the grid type, because of the better electrical contact at the electrode.

One of the experiments shown illustrated an arrangement of this kind. The filament of a small 6-volt lamp was focussed upon a selenium cell with a sensitive area of 1 mm.², by means of two lenses 4 cm. in diameter, over the length of the lecture table. The light was interrupted by means of a phonic wheel rotating close to the lamp. The fluctuating current in the selenium cell was amplified and made audible throughout the theatre by means of a loud-speaker.

Another experiment illustrated the advantages of balancing two selenium cells in a Wheatstone bridge arrangement. By exposing the cells alternatively to illumination the balance was upset in opposite directions.

PUBLICATIONS OF THE PHYSICAL SOCIETY

THE SCIENTIFIC PAPERS
OF THE LATE
SIR CHARLES WHEATSTONE, F.R.S.
Demy 8vo, cloth. Price 12s.; to Fellows, 6s.

Uniform with the above.
THE SCIENTIFIC PAPERS OF
JAMES PRESCOTT JOULE, D.C.L., F.R.S.
Vol. I. 4 Plates and Portrait, price 18s.; to Fellows, 9s.
Vol. II. 3 Plates, price 12s.; to Fellows, 6s.

PHYSICAL MEMOIRS
PART I.—VON HELMHOLTZ, On the Chemical Relations of Electrical Currents. Pp. 110. *Price 6s.; to Fellows, 3s.*
PART II.—HITTORF, On the Conduction of Electricity in Gases; PULUJ, Radiant Electrode Matter. Pp. 222. *Price 12s.; Fellows, 6s.*
PART III.—VAN DER WAALS, On the Continuity of the Liquid and Gaseous States of Matter. Pp. 164. *Price 12s.; to Fellows, 6s.*

REPORT ON RADIATION AND THE QUANTUM THEORY
By J. H. JEANS, D.Sc., LL.D., F.R.S.
Second Edition.—*Price 7s. 6d.; to Fellows, 3s. 9d. Bound in Cloth, 10s. 6d.*

REPORT ON THE RELATIVITY THEORY OF GRAVITATION
By A. S. EDDINGTON, M.A., M.Sc., F.R.S.
Plumian Professor of Astronomy and Experimental Philosophy, Cambridge.
Third Edition.—*Price 6s.; to Fellows, 3s. Bound in cloth, 8s. 6d.; to Fellows, 6s.*

REPORT ON SERIES IN LINE SPECTRA
By A. FOWLER, F.R.S.
Professor of Astrophysics, Imperial College of Science, South Kensington, London.
Price to Non-Fellows, 12s. 6d.; to Fellows, 6s. 3d. Bound in cloth, 15s.; to Fellows, 9s.

THE TEACHING OF PHYSICS IN SCHOOLS
Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

METROLOGY IN THE INDUSTRIES
Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

DISCUSSION ON LUBRICATION
Price to Non-Fellows, 1s. 6d. net, post free 1s. 8d.

DISCUSSION ON ELECTRIC RESISTANCE. *Price 2s. 6d. net.*

DISCUSSION ON HYGROMETRY. *Price 5s. net.*

DISCUSSION ON IONISATION IN THE ATMOSPHERE. *Price to Non-Fellows, 3s.*

PROCEEDINGS
The "Proceedings" of the Physical Society can be obtained at the following prices:
Vol. I. (3 parts) bound cloth 22s. 6d.
Vols. II., IV., V., XXIII., XXV., XXVI., XXVII., XXVIII., XXIX., XXX. & XXXI.
    (5 parts each), cloth, 34s. 6d.
Vols. III., VI. to XII. & XXII. (4 parts each), bound cloth, 28s. 6d.
Vols. XIII. (13 parts, each containing Abstracts), bound cloth (without Abstracts), 70s. 6d.
Vols. XIV. & XV. (12 parts, each containing Abstracts), bound cloth (without Abstracts), 34s. 6d.
Vols. XVI. & XIX. (8 parts each), bound cloth, 52s. 6d.
Vols. XVII., XVIII. & XXI. (7 parts each), bound cloth, 46s. 6d.
Vols. XX. & XXIV. (6 parts), bound cloth, 40s. 6d.

Most of the parts can be purchased separately, price 6s., by post 6s. 3d. Fellows can obtain the *Proceedings* (in parts) for their personal use at half the above prices.

Owing to the small number of copies in stock the following parts of "Proceedings" cannot be obtained without consent of the Council:—Vol. I., all parts; Vol. II., Part 1; Vol. IV., Part 4; Vol. VI., Part 1; Vol. VII., Part 4; Vol. XI., Parts 2 and 3; Vol. XII., Part 1; Vol. XIII., Part 12; Vol. XIV., Part 11; Vol. XXIII, Part 2; Vol. XXXI., Part 5; Vol. XXXII., Parts 2, 3, 4, 5.

ABSTRACTS OF PHYSICAL PAPERS FROM FOREIGN SOURCES
Vols. I. (1895), II. (1896), III. (1897), 22s. 6d. each; Fellows, 11s. 3d.

Strong cloth cases for binding the "Proceedings," price 2s. 6d. each, post free.

BLAKESLEY, T. H. A Table of Hyperbolic Sines and Cosines. *Price 2s. 3d.; to Fellows, 1s. 2d.*
LEHFELDT, R. A. A List of Chief Memoirs on the Physics of Matter. *Price 3s.; to Fellows, 1s. 6d.*

Applications for the above Publications should be sent direct to
FLEETWAY PRESS LTD.,
3-9, DANE STREET, HIGH HOLBORN, LONDON, W.C.1.

CONTENTS.